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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

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NOVEMBER, 1911

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PHYSICAL REVIEW.

AN ABSOLUTE DETERMINATION OF THE MINIMUM IONIZING ENERGY OF AN ELECTRON, AND THE APPLICATION OF THE THEORY OF IONIZATION BY COLLISION TO MIXTURES OF GASES.

By Edwin S. Bishop.

THE theory of "ionization by collision" has been very beautifully worked out by J. S. Townsend and verified by him and others[1] for various gases at low pressures. The orignial purpose of these experiments was to submit the theory to a more rigid test by extending the observations to wide ranges of pressure, and by predicting, if possible, the electrical properties of a mixture of gases, the properties of the constituent pure gases being known.

Professor Townsend has shown that an ion in a sufficiently strong electric field will acquire sufficient kinetic energy between some of the collisions with the molecules to produce new ions from the neutral molecules. He has further shown that if the field strength is not too high, it is only the negative ion which is effective in producing new ones. Under these conditions, if we have n_0 ions set free by the action of the ultra-violet light at the negative plate of the two parallel plates between which the electric field is established, then the number of ions n reaching the positive plate is given by the formula

$$n = n_0 e^{\alpha d} \qquad (1)$$

where e is Napier's base, α is the number of ions (either positive or negative) produced by the collisions of a negative ion in passing through one centimeter of the gas, and d is the distance between the plates in

[1] Townsend, Nature, Vol. LXII., Aug. 9, 1900; Phil. Mag., Feb., 1901, June, 1902, Nov., 1903, March, 1905; Townsend and Kirkby, Phil. Mag., June, 1901; Townsend and Hurst, Phil. Mag., Dec., 1904; Hurst, Phil. Mag., April, 1906; Gill and Pidduck, Phil. Mag., Aug., 1908.

centimeters. Townsend[1] has also shown that for large values of X/p (field strength in volts per cm. ÷ pressure), the positive ions also produce new ones by collision, so that if β is the number of ions (either positive or negative) produced by a positive ion in passing through one centimeter of the gas, then the number of ions n which reach the positive plate is given by the equation

$$n = \frac{n_0(\alpha - \beta)e^{(\alpha-\beta)x}}{\alpha - \beta e^{(\alpha-\beta)x}}.$$

Inasmuch as all the experiments herein described were carried out at pressures much higher than those used by Townsend, the values of X/p are comparatively small, and consequently the first formula $n = n_0 e^{\alpha x}$ was found to satisfy all of the experimental data.

DESCRIPTION OF APPARATUS.

The apparatus which was used for finding the conductivity between two parallel plates is shown in Fig. 1. The conductivity was started

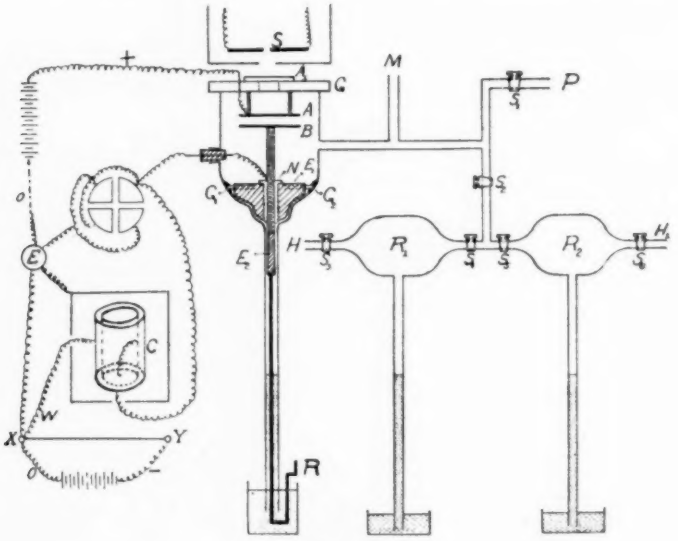

Fig. 1.

by means of ultra-violet light falling upon the aluminum plate B, from the spark S, which consisted of two zinc electrodes. The spark was maintained by the discharge of four Leyden jars across the secondary of a Scheidel induction coil. The Scheidel coil was run on an alternating current from a rotary generator, the current which supplied the coil being

[1] Townsend, Phil. Mag., Nov., 1903.

kept constant throughout a set of readings as well as the speed of the rotary generator. In this way the intensity of the light from the spark could be kept at any desired value, and a set of readings could be reproduced at any time with an error of less than three per cent. The ionization of the gas took place between the plates A and B, which were five centimeters in diameter. Plate G was a piece of heavy plate glass with a circular aperture one centimeter in diameter, over which was cemented the quartz plate A_1. Plate A was a silvered quartz plate with lines ruled every four tenths of a millimeter over an aperture one centimeter in diameter, to allow the passage of the light. Plate B was made of aluminum, mounted on a metallic screw which turned in the metal nut N, by means of the rod R. E_2 was a piece of ebonite about three centimeters long inserted between the screw and the rod to secure insulation. E_1 was an ebonite base which was held firmly in place by inserting into it glass rods, G_1, G_2 (G_3 not shown in diagram), which were fastened to the sides of the glass ionizing chamber with cæmentium. Plate B was made as accurately parallel with plate A as was possible before fastening plate G, which carried plate A by means of pillars, to the ionizing chamber. Plate G was sealed to the apparatus with De Khotinski cement. Connection was made between the plate B and the electrometer by a wire passing from the nut N through an amber plug in the side of the ionizing chamber. C was a cylindrical condenser the inside of which was connected to the plate B and the electrometer, and the outside of which was connected by the slide wire W to a high resistance bridge XY to which was applied about six volts for the measurement of the smaller currents. The positive potentials applied to the plate A were obtained from storage batteries, and varied from fifty to thirty-four hundred volts, depending on the pressure of the gas. These voltages were read on one of four Kelvin and White static voltmeters which ranged from 0 to 90 volts, 0 to 360 volts, 0 to 900 volts, 0 to 1,600 volts respectively. The voltmeters were first accurately calibrated by Mr. Kadesch and myself with a standard voltmeter, and were accurate to within one half per cent. A Gaede pump attached at P served to evacuate the whole system. A MacLeod gauge attached at M was used to measure pressures up to four centimeters. The higher pressures were read directly from a mirror scale placed back of the tube M. R_1 and R_2 were glass reservoirs of about 500 c.c. capacity which contained the gases to be studied. R_1 was kept nearly filled with hydrogen throughout the course of the experiments. The hydrogen used was produced by the electrolysis of phosphoric acid in distilled water. It was then bubbled through an alkaline solution of pyrogallic acid to remove the oxygen and passed into three

drying tubes which contained caustic potash, calcium chloride, and phosphorous pentoxide respectively. All connections for this system were glass-sealed joints. After staying in the drying tubes for at least eight hours, the hydrogen was admitted to the reservoir R_1. The reservoir R_2 contained either air or else carbon dioxide, depending on the gas or mixture being studied. The carbon dioxide was carefully prepared and dried, as was also the air. The volumes of R_1 and R_2 were accurately determined before setting up the apparatus by weighing each empty and then filled with water at a known temperature. The barometer tubes leading down from R_1 and R_2 were each provided with a scale so that by knowing the change in pressure and volume of each reservoir, the quantity of each gas which was admitted to the ionizing chamber was known with an accuracy of one tenth per cent. The ionizing chamber for each set of observations was first exhausted to a pressure of one thousandth of a millimeter or less, with the Gaede pump, and then filled with a fresh supply of gas to a pressure which was always about ten centimeters greater than that for which the observations were to be taken. The ionizing chamber was then exhausted to the desired pressure. By this means, the traces of any gas left could never have been more than one hundred-thousandth part of the whole, and would therefore produce an entirely negligible effect. The apparatus was tested several times during the course of the experiments and when exhausted to one thousandth of a millimeter or less, the increase of pressure during three hours, the time required to make a set of observations, was never found to be more than two thousandth of a millimeter, so that any impurities in the gas arising from leakage or occluded gases in the apparatus must have produced an entirely negligible effect.

METHOD OF OBSERVING.

To make an observation the desired positive potential was applied to plate A; plate B, the pair of quadrants to which B was connected, and the inside cylinder of the capacity were earthed, and the slide wire W was at X (always zero potential). The spark was then started, plate B and its connecting system unearthed, and the time noted with a stop watch which was required for B to acquire a positive charge which could be just balanced by sliding the wire W of the inductive balance from X to Y. By this means the deflection of the electrometer could be kept within a fraction of a millimeter of its zero point, at a distance of 150 cm., during an observation. Three trials were usually made for an observation, the individual trials seldom varying by more than two per cent. from the mean.

To obtain a set of data the above process was repeated for several positive potentials applied to plate A, starting with potentials considerably less than was required to produce ionization by collision and continuing up to voltages which produced ionization currents that could just be balanced on the bridge.

If we let V represent the P.D. across the inductive balance, c the capacity of the condenser, electrometer, and plate B, and t the time in seconds required for plate B to acquire the potential V, then the currents through the gas will be proportional to cV/t. Since the capacity is constant the currents will be proportional to V/t, and these are the values for the current which are given in Figs. 2 to 10 inclusive.

It will be noted from the figures that the so-called saturation current slowly increases with the potential applied to plate A until the field strength (potential ÷ distance between plates) is sufficient to produce new ions by collision, at which point the increase in current becomes much greater. Before that field strength is reached, equal small increments in current are produced by equal large increments in the potentials applied to plate A, giving a straight line when plotted up to the point where ionization by collision begins. This gradual increase in the so-called saturation current is probably due to two causes. First, as the field strength is increased, fewer of the electrons released by the action of the light are discharged back to the plate, and second, the energy of emission of the electron from the plate added to the energy it received

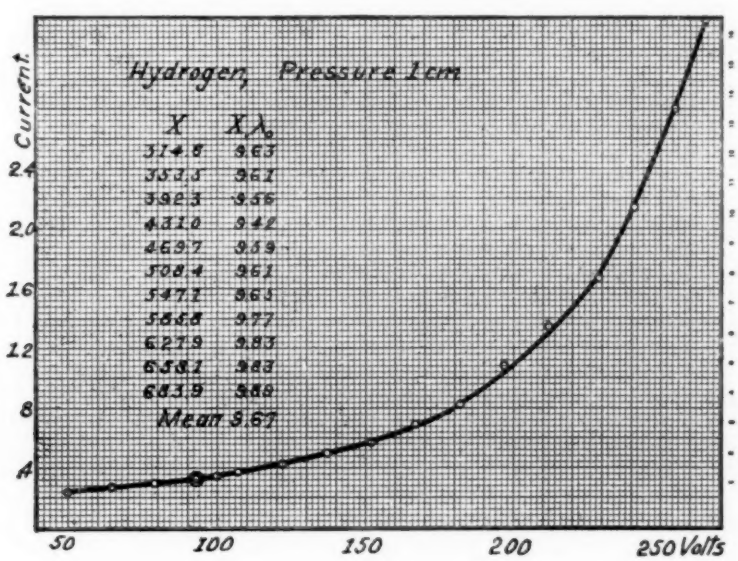

Fig. 2.

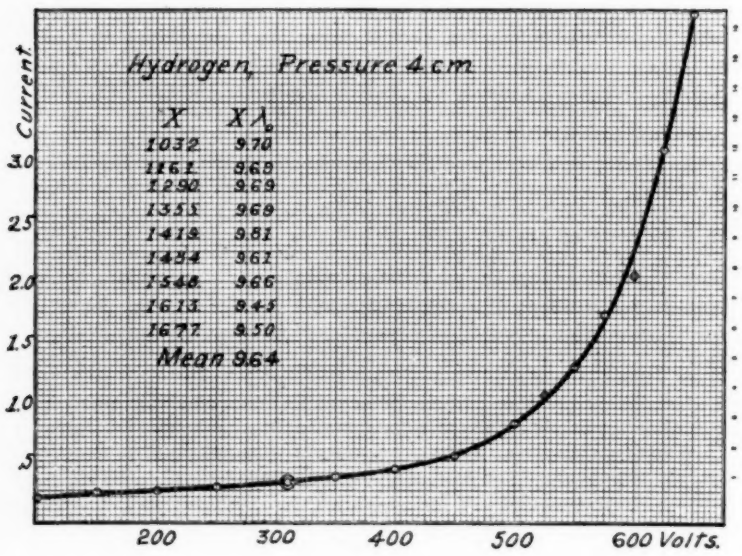
Hydrogen, Pressure 4 cm.
X Xλ₀
1032 9.70
1161 9.68
1290 9.69
1355 9.69
1419 9.81
1454 9.61
1548 9.66
1613 9.45
1677 9.50
Mean 9.64
Current.
3.0
2.5
2.0
1.5
1.0
.5
200
300
400
500
600 Volts.

Fig. 3.

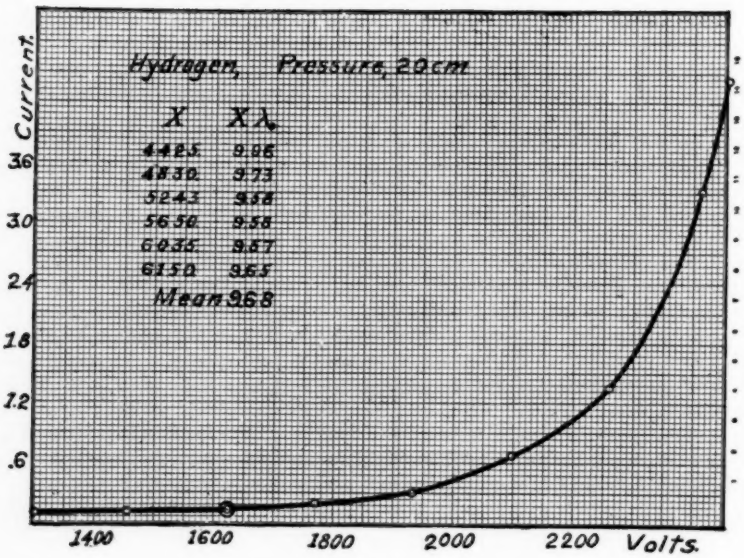
Hydrogen, Pressure, 2.0 cm.
X Xλ₀
4425 9.86
4830 9.73
5243 9.58
5650 9.58
6035 9.87
6150 9.65
Mean 9.68
Current.
3.6
3.0
2.4
1.8
1.2
.6
1400
1600
1800
2000
2200 Volts.

Fig. 4.

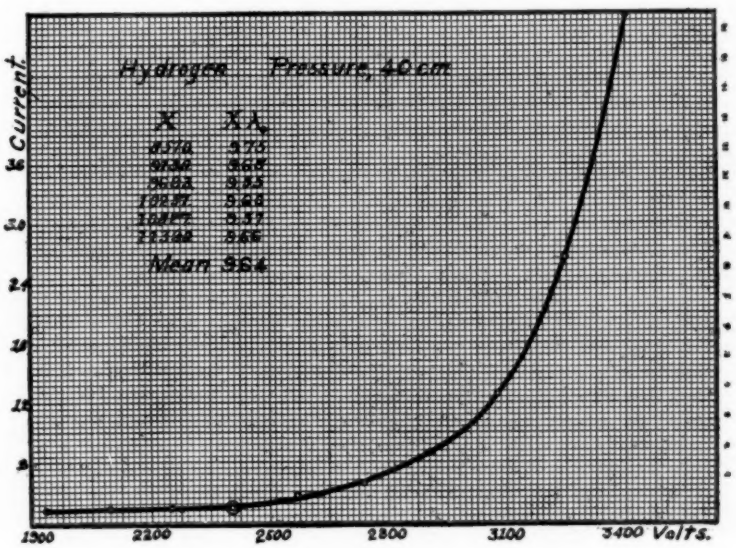
Hydrogen Pressure, 4.0 cm.
X Xλ
Mean 9.64
Current.
1300
2200
2500
2800
3100
3400 Volts.

Fig. 5.

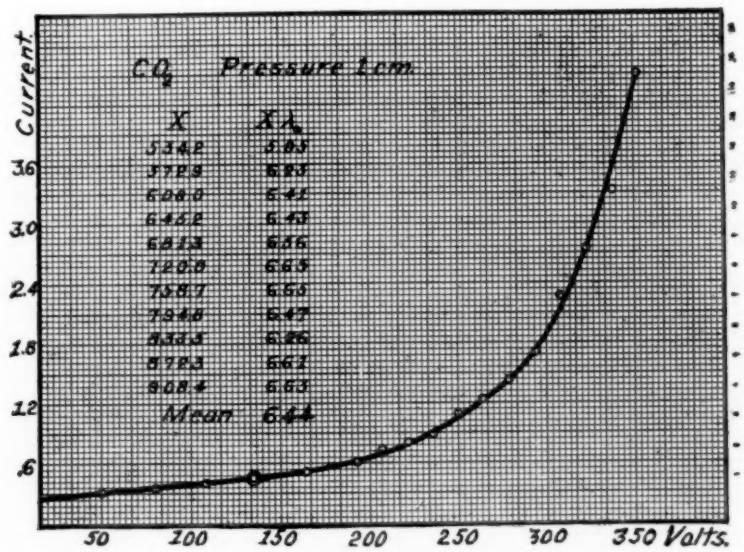
CO_2 Pressure 1 cm.
X Xλ
Mean 6.44
Current.
50
100
150
200
250
300
350 Volts.

Fig. 6.

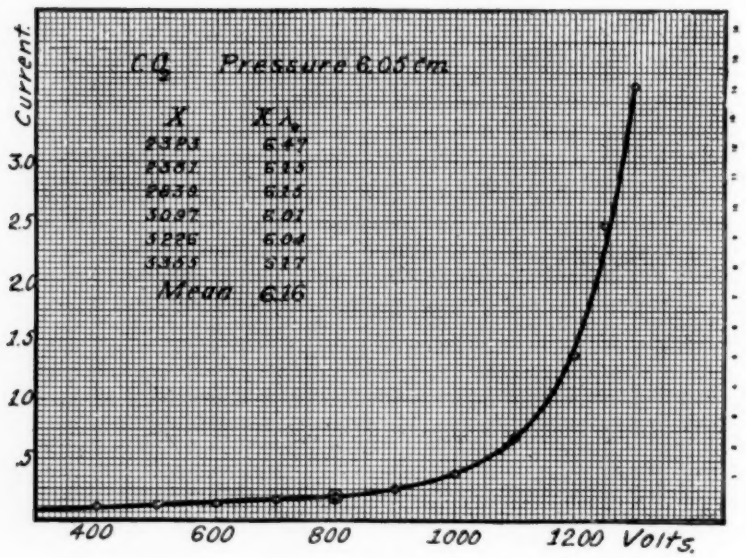
Current.
CO_2 Pressure 6.05 cm.
X
$X\lambda_0$
2323
6.47
2361
6.15
2838
6.15
3097
6.01
3226
6.04
3363
6.17
Mean 6.16
3.0
2.5
2.0
1.5
1.0
.5
400
600
800
1000
1200 Volts.

Fig. 7.

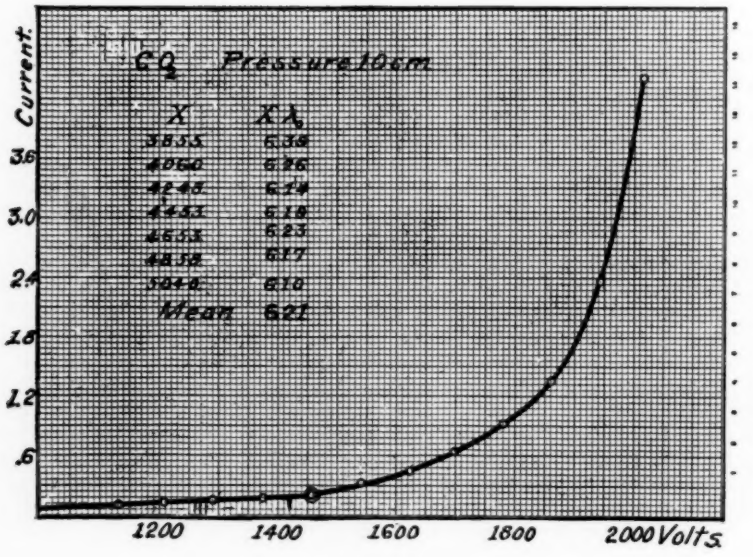
Current.
CO_2 Pressure 10 cm.
X
$X\lambda_0$
3855
6.38
4060
6.26
4245
6.19
4453
6.18
4655
6.23
4858
6.17
5044
6.10
Mean 6.21
3.6
3.0
2.4
1.8
1.2
.6
1200
1400
1600
1800
2000 Volts.

Fig. 8.

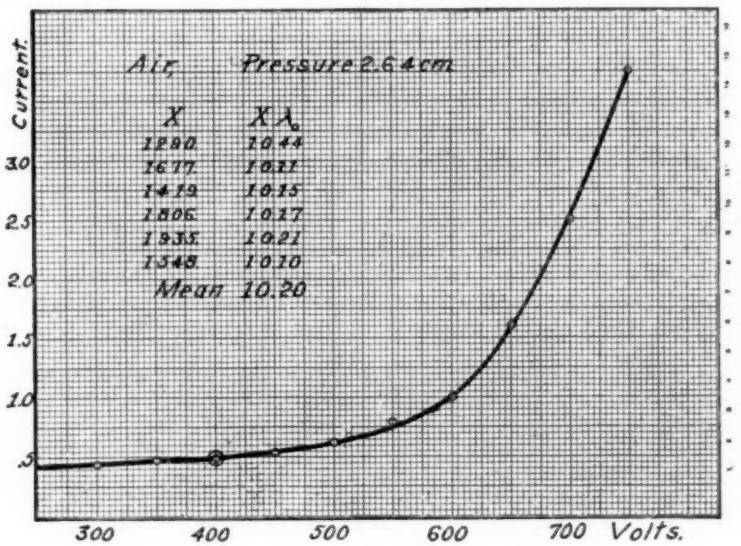
Air. Pressure 2.64 cm.
X
1290
1677
1419
1806
1935
1348
Mean
Xλ₀
10.44
10.11
10.15
10.17
10.21
10.10
10.20
Current.
3.0
2.5
2.0
1.5
1.0
.5
300
400
500
600
700
Volts.

Fig. 9.

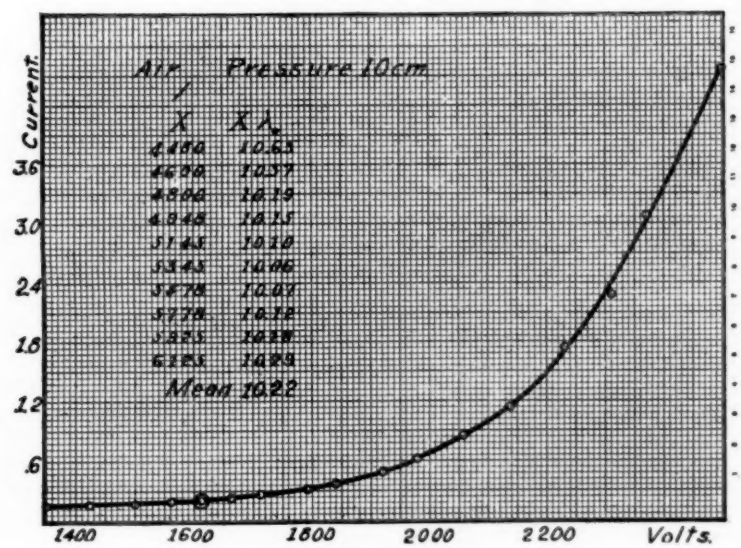
Air. Pressure 10 cm.
X
2480
4698
4806
4848
5145
5343
5478
5778
5925
6165
Mean
Xλ₀
10.65
10.57
10.19
10.15
10.10
10.06
10.07
10.12
10.18
10.29
10.22
Current.
3.6
3.0
2.4
1.8
1.2
.6
1400
1600
1800
2000
2200
Volts.

Fig. 10.

TABLE I.

Hydrogen.

Pressure 1 cm. $n_0 = .345$, $d = .3875$ cm.				Pressure 1.9 cm. $n_0 = .318$, $d = .3875$ cm.			
X	n/n_0	α	X'	X	n/n_0	α	X'
314.8	1.245	.544	312.0	451.6	1.11	.269	472.6
353.5	1.435	.932	356.3	516.1	1.23	.534	521.5
392.3	1.640	1.277	390.1	580.6	1.45	.959	583.1
431.0	2.010	1.802	435.3	645.2	1.74	1.430	639.9
469.7	2.390	2.249	469.8	709.7	2.29	2.138	714.0
508.4	3.130	2.945	518.4	774.2	2.97	2.810	775.2
547.1	3.880	3.499	554.9	838.7	4.03	3.597	840.9
585.8	4.840	4.070	590.0	903.2	5.66	4.472	906.9
621.9	6.200	4.710	626.6	967.7	8.01	5.370	971.3
658.1	8.120	5.404	664.5	1,032.2	11.48	6.292	1,031.3
683.9	9.920	5.923	691.0	1,058.0	13.43	6.697	1,057.4
Pressure 4 cm. $n_0 = .323$, $d = 3875$ cm.				**Pressure 5 cm. $n_0 = .481$, $d = .3875$ cm.**			
1,032	1.32	.716	1,025	1,161	1.16	.383	1,166
1,161	1.69	1.360	1,157	1,290	1.45	.962	1,294
1,290	2.51	2.375	1,273	1,419	1.83	1.564	1,398
1,355	3.26	3.050	1,352	1,548	2.61	2.476	1,529
1,419	3.92	3.525	1,404	1,677	4.17	3.685	1,676
1,484	5.32	4.314	1,485	1,806	6.65	4.889	1,805
1,548	6.34	4.766	1,528	1,871	9.16	5.716	1,887
1,613	9.60	5.837	1,625				
1,677	13.10	6.632	1,694	**Pressure 10 cm. $n_0 = .176$, $d = .3875$ cm.**			
Pressure 20 cm. $n_0 = .123$, $d = .4$ cm.				2,323	1.38	.831	2,350
4,425	1.56	1.112	4,546	2,581	1.94	1.710	2,547
4,830	2.43	2.220	4,838	2,839	3.31	3.089	2,789
5,243	5.32	4.179	5,239	3,097	6.40	4.790	3,035
5,650	10.97	5.981	5,548	3,226	9.37	5.773	3,161
6,035	26.90	8.220	5,884	3,355	14.27	6.852	3,293
6,150	35.90	8.942	5,982	3,484	23.50	8.13	3,436
Pressure 30 cm. $n_0 = .130$, $d = .3$ cm.				**Pressur o cm. $n_0 = .141$. $d = .3$ cm.**			
6,543	1.67	1.709	6,696	8,570	1.87	2.086	8,877
6,997	2.43	2.960	6,977	9,130	2.68	3.286	9,164
7,503	3.84	4.485	7,264	9,693	4.93	5.318	9,568
8,020	6.96	6,467	7,586	10,257	9.15	7.379	9,919
8,580	13.65	8.702	7,906	10,827	18.78	9.765	10,284
9,100	33.98	11.740	8,293	11,390	36.09	11.940	10,586

from the field would be sufficient to ionize at the first impact, although the field strength were below the minimum ionizing field strength. When, however, the field strength attains such a value that the electron acquires

sufficient energy between some of the impacts to ionize, then the current will increase rapidly for small increases in field strength. Thus the potential (or field strength) at which ionization by collision begins is obtainable either from the data or the curves and these points are indicated on the curves by two concentric circles. All the data for these experiments is obtainable from the curves, the abscissæ representing the number of volts applied to plate A and the ordinates representing the corresponding values of V/t (volts applied to inductive balance $XY \div$ time for plate B to acquire the potential V). The tables accompanying the curves show the values obtained for the ionizing energy for corresponding values of the field strength. The value of n_0 in all cases was taken as the value of the current at these doubly circled points, and n was the value of the current for any higher potential. The method of determining the minimum ionizing energy $X\lambda_0$ (free fall of the electron in volts) is given in the next general heading of this paper.

The values of α for various field strengths X were then calculated

TABLE II.

Carbon Dioxide.

Pressure 1 cm. $n_0 = .453$, $d = .3875$ cm.			
X	n/n_0	α	X'
534.2	1.60	1.213	553.7
572.9	1.79	1.503	583.8
609.0	1.95	1.733	605.4
645.2	2.43	2.291	656.9
681.3	2.73	2.591	682.4
720.0	3.16	2.970	713.2
758.7	3.75	3.412	747.4
794.8	5.01	4.158	801.9
833.5	6.07	4.653	836.3
872.3	7.33	5.141	861.3
908.4	9.93	5.925	898.0
Pressure 10 cm. $n_0 = .204$, $d = .4$ cm.			
3,855	1.60	1.175	3,983
4,060	2.16	1.975	4,146
4,248	3.19	2.900	4,329
4,453	4.51	3.766	4,474
4,653	6.62	4.725	4,621
4,858	11.60	6.120	4,819
5,040	21.66	7.680	5,023

Pressure 3.53 cm. $n_0 = .197$, $d = .3875$ cm.			
X	n/n_0	α	X'
1,548	1.59	1.197	1,558
1,806	3.22	3.017	1,810
1,935	5.00	4.152	2,009
2,064	7.97	5.357	2,066
2,194	12.48	6.508	2,177
2,258	18.73	7.554	2,272
Pressure 5 cm. $n_0 = .240$, $d = .3875$ cm.			
2,052	1.60	1.213	2,122
2,263	2.53	2.395	2,316
2,472	4.17	3.683	2,491
2,681	7.04	5.038	2,655
2,888	14.80	6.947	2,862
2,942	18.75	7.556	2,923
Pressure 6.05 cm. $n_0 = .189$, $d = .3875$ cm.			
2,323	1.31	.697	2,407
2,581	2.04	1.840	2,634
2,839	3.64	3.334	2,865
3,097	7.25	5.112	3,096
3,226	13.07	6.624	3,272
3,355	19.21	7.618	3,380

from the formula $n = n_0 e^{ad}$, and are given in Tables I., II., and III. The computed values of the field strengths X' required to produce the same current, *i. e.*, the same value of n/n_0 are given in the last columns of the same tables. The method of obtaining these will be described in a later section.

TABLE III.

Air.

Pressure 2.64 cm. $n_0 = .498$, $d = .3875$ cm.				Pressure 10 cm. $n_0 = .197$, $d = .4$ cm.			
X	n/n_0	a	X'	X	n/n_0	a	X'
1,290	1.25	.576	1,287	4,480	1.56	1.112	4,576
1,419	1.59	1.197	1,419	4,600	1.86	1.551	4,709
1,548	2.00	1.789	1,522	4,800	2.46	2.250	4,892
1,677	3.21	3.009	1,699	4,948	3.13	2.852	5,033
1,806	5.02	4.163	1,843	5,145	4.28	3.635	5,200
1,935	7.53	5.210	1,959	5,345	5.78	4.386	5,348
Pressure 4.92 cm. $n_0 = .155$, $d = .3875$ cm.				5,578	8.83	5.445	5,542
				5,778	11.57	6.114	5,656
				5,925	15.58	6.857	5,778
2,323	1.43	.914	2,358	6,125	23.20	7.851	5,933
2,581	2.14	1.963	2,594	Pressure 5.27 cm. $n_0 = .205$, $d = .3875$ cm.			
2,839	3.53	3.254	2,824				
3,097	6.64	4.885	3,068				
3,226	10.13	5.969	3,214	2,323	1.20	.471	2,365
3,354	16.25	7.187	3,365	2,581	1.68	1.332	2,613
3,419	21.60	7.920	3,452	2,839	2.48	2.344	2,825
				3,097	4.02	3.592	3,042
				3,355	7.90	5.334	3,301
				3,484	15.90	7.130	3,535

DETERMINATION OF THE MINIMUM IONIZING ENERGY.

Mr. Bergen Davis[1] has deduced a theory for the minimum kinetic energy which a negative ion must have in order to ionize a molecule by impact. He has shown that if α is the number of ionizing impacts which a negative ion makes in passing through one centimeter of a gas, l is the mean free path of the ion, and λ_0 is the minimum path which results in ionization, then the number of ionizing impacts is given by the following equation:

$$\alpha = \frac{1}{l} e^{-\frac{\lambda_0}{l}} \left[1 + \frac{\lambda_0}{l} e^{\frac{\lambda_0}{l}} Ei\left(-\frac{\lambda_0}{l}\right) \right],$$

which may be written

$$\alpha l = e^{-\frac{\lambda_0}{l}} + \frac{\lambda_0}{l} Ei\left(-\frac{\lambda_0}{l}\right). \qquad (2)$$

[1] Bergen Davis, PHYSICAL REVIEW, Jan., 1907.

The values of the ponential integral $Ei(-\lambda_0/l)$ were obtained by him from tables by Dr. W. Laska (Sammlung von Formeln). The values of αl and the corresponding values of λ_0/l as computed by Davis are given in Table IV.

TABLE IV.

λ_0/l	αl	λ_0/l	αl	λ_0/l	αl
.04	.8536	.4	.3893	4	.0032
.06	.804	.6	.2762	5	.00099
.1	.7247	.8	.2008	6	.00032
.14	.656	1.	.1485	7	.000142
.2	.574	1.5	.0731	8	.000034
.25	.518	2.	.0375	9	.0000114
.3	.496	3.	.0106	10	.00000387

These values were plotted on three large curves about thirty centimeters each way, using the values of λ_0/l for the abscissæ and the corresponding values of αl for the ordinates. By referring to these curves the value of λ_0/l corresponding to any experimental value of αl could be interpolated within a fraction of one per cent.

The values of the mean free paths of hydrogen, carbon dioxide, and air at 76 cm. pressure and 23° C. in all these experiments were taken to be .0000185, .00000654, and .00000983 cm. respectively. At other pressures the mean free paths were taken inversely proportional to the pressure. In all cases the mean free path of the negative ion (electron) was taken to be 5.65 times the mean free path of the gas molecule at that pressure. If the electron is negligible in size, then its mean free path would be four times that of the gas under the same velocity conditions. Since, however, the electron when in fields sufficiently strong to cause it to ionize, moves with a velocity of order higher than that of the molecules,[1] its mean free path should be $\sqrt{2}$ times as great on that account.[2] Thus the mean free path of the electron in a gas should be $4\sqrt{2}$ times the mean free path of the molecule of the gas.[1]

Using this value of l and the experimentally determined values of α (see Tables I., II., III.), the values of λ_0/l corresponding to the values of αl for the various field strengths were found from the curves previously described. The minimum ionizing energy expressed in the number of volts through which the electron must freely fall would then be

$$\text{Energy (Volts)} = \frac{Xl\lambda_0}{l} = X\lambda_0.$$

[1] From $e/m = 5.6 \times 10^{17}$ E.S.U. and equating $\frac{1}{2}mv^2$ to $Xe\lambda_0$, the minimum ionizing velocities of the electron in hydrogen, carbon dioxide, and air are 10^3, 4.3×10^3, and 4×10^3 times as great as the velocities of agitation of the molecules of these gases respectively.

[2] J. C. Maxwell, Phil. Mag., Ser. 4, Vol. 19, p. 29, 1860.

The data for the different gases is shown by the curves of Figs. 2 to 10 inclusive, and the results for $X\lambda_0$ corresponding to different values of X are shown in the tables accompanying those figures. A summary of all the values of $X\lambda_0$ for the different gases and pressures is given in Table V.

TABLE V.

Hydrogen.		Carbon Dioxide.		Air.	
Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$
1	9.67	1	6.44	2.64	10.20
1.9	9.59	3.53	6.28	4.92	10.22
4	9.64	5	6.17	5.27	10.18
5	9.68	6.05	6.16	10	10.22
10	9.72	10	6.21		
20	9.68				
30	9.67				
40	9.64				

In finding the final mean of $X\lambda_0$ (Table VI.) for the different gases the above values of $X\lambda_0$ were given weights proportional to the pressures, since the accuracy of several observations increases with the pressure. The value of the minimum ionizing energy expressed in ergs would be

$$\text{Energy (Ergs)} = \frac{X\lambda_0}{300} \cdot e,$$

where e is the value of the elementary charge on the electron. The value of e used here was 4.89×10^{-10}, which was the value recently determined by Professor R. A. Millikan[1] by experiments on oil drops and which has been verified by E. Regener.[2]

TABLE VI.

Gas.	$X\lambda_0$ (Volts).	$Xe\lambda_0$ (Ergs).
Hydrogen	9.66	1.58×10^{-11}
Carbon dioxide	6.21	1.01×10^{-11}
Air[3]	10.21	1.67×10^{-11}

[1] R. A. Millikan, Science, Vol. XXXII., Sept. 30, 1910, and PHYSICAL REVIEW, April, 1911.

[2] E. Regener, Physikalische Zeitschrift, Feb. 15, 1911.

[3] The mean free paths used in determining the above values were taken from Meyer's Kinetic Theory. The mean free path of air at 23° C., computed from the most probable value of the coefficient of viscosity as given by R. A. Millikan in the PHYSICAL REVIEW, April, 1911, p. 386, is 5 per cent. less. This value of the mean free path of air gives a value for the ionizing energy which is 4 per cent. less than the above, or 9.8 volts. It will be noticed that O. V. Baeyer's value of 10 volts, which is the most direct determination which has been made, lies between these two values. This would indicate that Jean's correction for the persistence of velocities is not here needed.

Lenard,[1] by a very direct method obtained 11 volts for the ionizing energy of air, and O. v. Baeyer[2] by a similar direct method obtained 10 volts. For a review of other work on this subject the reader is referred to an article by Dr. Kleeman, published in the Proceedings of the Royal Society, June 9, 1910.

Relative Ionizing Energy for the Different Gases.

If we plot the field strengths corresponding to the doubly circled points of Figs. 2 to 18 inclusive as ordinates, and the corresponding pressures as abscissæ, we obtain the straight lines shown in Fig. 19.

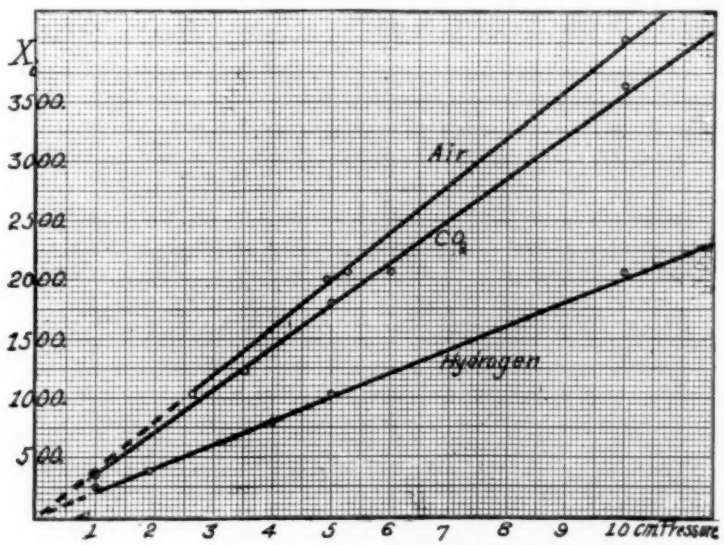

Fig. 11.

These are the minimum ionizing field strengths and are denoted by X_i. From these curves the very important law follows, that the minimum ionizing field strength for any gas is directly proportional to the pressure, or for any gas

$$\frac{X_i}{p} = \text{Cst.} \qquad (3)$$

This equation satisfies the conditions at least for pressures above one centimeter. The straight lines are produced as dotted lines back to the origin merely to show that the law is a direct proportion. However, this law, as is well known, does not hold at low pressures and the experi-

[1] Lenard, Drude's Ann. der Phys., Vol. 8, 1902.

[2] O. v. Baeyer, Verhandlungen der Deutschen Physikalischen Gesellschaft, Vol. 10, p. 100, 1908.

mental data would not follow the dotted portions of the curves, but would curve up as very low pressures were approached, the minimum ionizing field strength increasing very rapidly for high vacua. The straight line for hydrogen does not show the results for pressures of 20 and 40 centimeters. The results may be obtained from Figs. 4 and 5, X_i being equal to V/d (volts applied to plate A corresponding to doubly circled points ÷ distance d between the plates). These points fall on the straight line for hydrogen produced. Thus the law $X_i/p = \text{Cst}$ has been verified up to 40 cm. pressure for hydrogen, and up to 10 cm. pressure for each of the gases, air and carbon dioxide. This constant was found to be 200 volts per cm. per cm. of pressure for hydrogen, 400 for air,[1] and 356 for carbon dioxide. In obtaining these values the mean of X_i/p for the different pressures was taken, each determination being given a weight proportional to the pressure of the gas.

First Method—Relative Energy: If the mean free path of the electron were the same in two gases, the relative ionizing energy of these gases would be

$$\frac{E_1}{E_2} = \frac{X_{i_1}}{X_{i_2}}, \tag{4}$$

where E_1 and E_2 are the minimum ionizing energies of the first and second gases respectively, and X_{i_1} and X_{i_2} are the corresponding minimum ionizing field strengths. But the ratio of the mean free paths of the electron in the two gases is the same as the ratio of the mean free paths of the molecules of the two gases, if the electron is negligible in size in comparison to the molecule. Since the energy acquired by the electron between impacts in the two gases is proportional to the mean free paths L_1 and L_2 of the gases, therefore the right hand member of Eq. (4) must be multiplied by this ratio. Hence we have for any two gases

$$\frac{E_1}{E_2} = \frac{X_{i_1}}{X_{i_2}} \cdot \frac{L_1}{L_2}. \tag{5}$$

For air and hydrogen,

$$\frac{E_A}{E_H} = \frac{400}{200} \cdot \frac{.00000983}{.0000185} = 1.063.$$

For air and carbon dioxide,

$$\frac{E_A}{E_{CO_2}} = \frac{400}{356} \cdot \frac{.00000983}{.00000654} = 1.689.$$

[1] P. J. Kirkby, Phil. Mag., Feb., 1902, p. 222, states that the smallest value of X/p which gives an appreciable value of α is 40. This corresponds to X/p equal to 400 here since the pressure he used was given in millimeters.

For hydrogen and carbon dioxide,

$$\frac{E_H}{E_{CO_2}} = \frac{200}{356} \cdot \frac{.0000185}{.00000654} = 1.589.$$

Second Method—Relative Energy: The fact that the minimum ionizing energy remains constant at all pressures, taken in connection with the law $X_1/p = \text{Cst}$, shows that the mean free path of the electron in a gas must be inversely proportional to the pressure of the gas. Hence in order to make the mean free path l of the electron the same in two gases, all we have to do is to make the pressures of the two gases proportional to the mean free paths of the gases, *i. e.*, $p_1/p_2 = L_1/L_2$.

If we obtain the ionization curves for these pressures (see Figs. 12

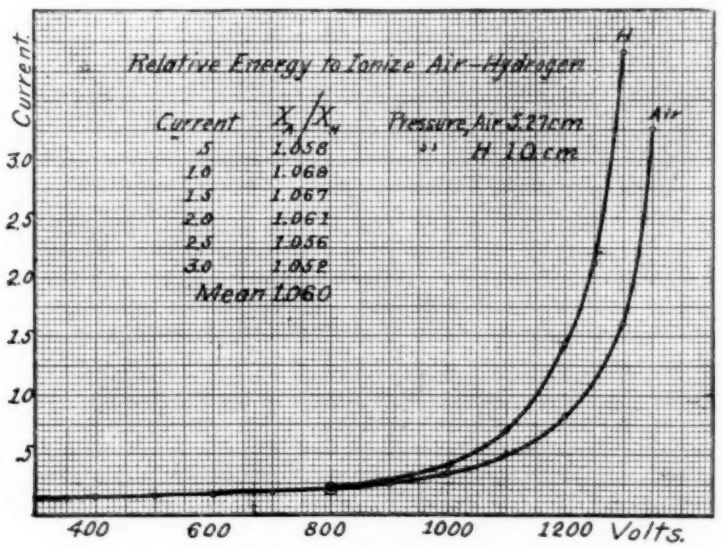

Fig. 12.

and 13) in the following manner, we shall have the necessary data for determining the relative ionizing energy of the two gases. Accordingly the spark was adjusted so that the value of n_0 was the same in the two gases, *i. e.*, the currents were made the same for the minimum ionizing field strength in each gas. This was done in some cases by changing the intensity of the spark, and in others by adjusting the distance of the spark above the plate.

Since we have n_0 the same in both gases, it is clear that if we take two points on the two curves where n is the same, *i. e.*, where the ionization currents are equal, then α, the number of ions produced by collision in each gas, must be the same. Having n_0, α, and l the same for both gases

their relative energy must be the ratio of the field strengths of any two points on the curves for which n is the same, for since the distance d between the plates was the same for both gases, the relative ionizing

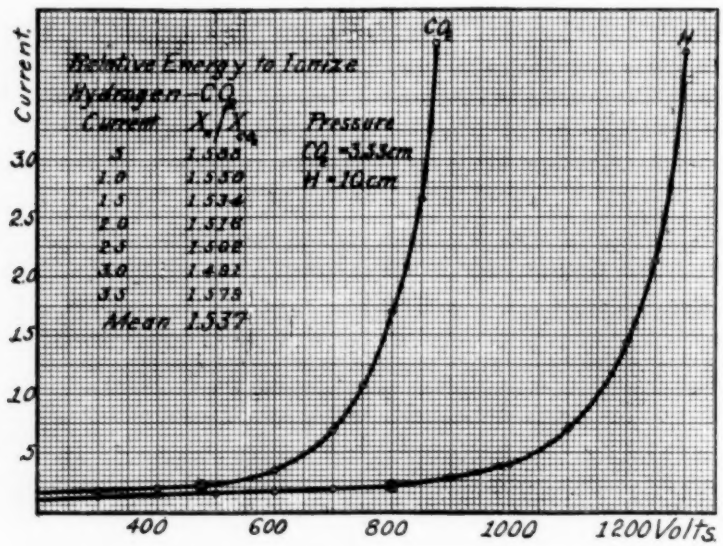

Fig. 13.

energy must be simply the ratio of the positive potentials V, applied to the plate A, or

$$\frac{E_1}{E_2} = \frac{V_1}{V_2}, \tag{6}$$

when

$$\frac{p_1}{p_2} = \frac{L_1}{L_2}$$

and n_0, α, l, and d are the same for both gases.

For air and hydrogen see Fig. 12 and table accompanying it. Here $E_A/E_H = 1.060$.

For hydrogen and carbon dioxide see Fig. 13 and accompanying table. Here $E_H/E_{CO_2} = 1.537$.

No data were taken by this method for comparing air and carbon dioxide.

Third Method—Relative Energy: A third method for obtaining the relative ionizing energy is by comparing the absolute values given in Table VI. While this is not a direct method, it serves somewhat as a check on the absolute values there given, since it gives the same relative ionizing energy as the first two methods.

For air and hydrogen $\frac{E_A}{E_H} = \frac{10.21}{9.66} = 1.057$.

For air and carbon dioxide, $\frac{E}{E_{CO_2}} = \frac{10.21}{6.21} = 1.644$.

For hydrogen and carbon dioxide, $\frac{E_H}{E_{CO_2}} = \frac{9.66}{6.21} = 1.556$.

For purposes of comparison the results of the three methods are given in Table VII.

TABLE VII.

Relative Ionizing Energies.

	E_A/E_H	E_A/E_{CO_2}	E_H/E_{CO_2}
First method	1.063	1.689	1.589
Second method	1.060	No data.	1.537
Third method	1.057	1.644	1.556

METHOD OF COMPUTING THE FIELD STRENGHTS REQUIRED TO PRODUCE A GIVEN CURRENT IN A PURE GAS.

Professor Townsend has shown that for small values of X/p

$$\frac{\alpha}{p} = F\left(\frac{X}{p}\right), \tag{7}$$

and that when X/p becomes large enough so that the positive as well as the negative ions produce new ones by collision

$$\frac{\beta}{p} = \phi\left(\frac{X}{p}\right), \tag{8}$$

where β is the number of ions (either positive or negative) produced by the collisions of a positive ion in passing through one centimeter of the gas.

In the present work the values of X/p are small compared to those used by Townsend, because of the fact that much higher pressures were used in this work than in his. According to his curves showing the relation between β/p and X/p, the values of β in the present experiments would be entirely negligible. Also since the values of α obtained in these experiments (see Tables I., II., III.) gives a constant value of $X\lambda_0$ for all field strengths and pressures, it follows that in these experiments the positive ions could not have produced new ions by collision.

In order to show that α/p is some function of X/p all of the values of α/p and corresponding values of X/p (taken from Tables I., II., III.), for all of the points observed (see Figs. 2 to 10) were plotted on a large

scale, and the result is shown in Fig. 14, which is reduced to about one seventh of the original size. These points fall upon a smooth curve and consequently prove the existence of such a function. When they were plotted it was at once evident that these curves intercepted the X-axis at $X/p = X_i/p$, where X_i/p was the constant determined from Fig. 11

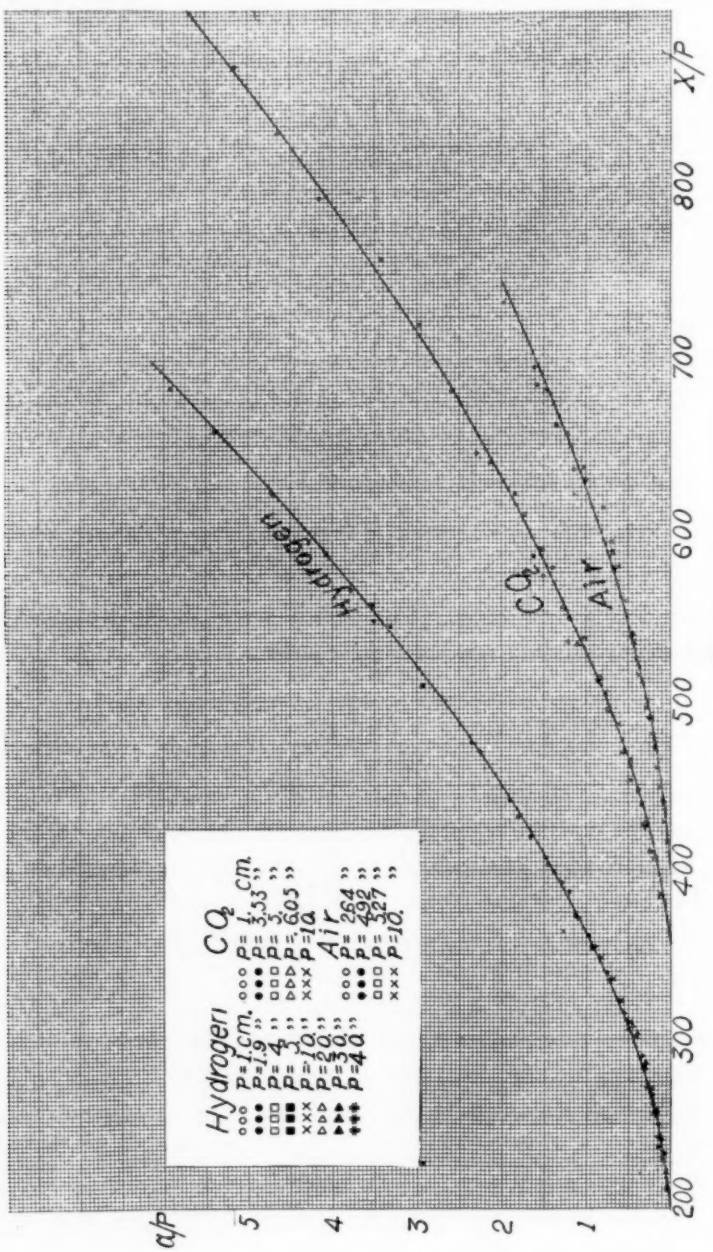

Fig. 14.

for the different gases. This would necessarily have to follow since α must be sensibly zero for field strengths which are very slightly less than the minimum ionizing field strength. Thus the function at once reduces to

$$\frac{\alpha}{p} = f\left(\frac{X}{p} - \frac{X_i}{p}\right), \tag{9}$$

where $X_i/p = 200$ for hydrogen, 356 for carbon dioxide, and 400 for air.

It was then found that all of the curves (Fig. 14) were satisfied by the general equation

$$\frac{\alpha}{p} = a\left(\frac{X}{p} - \frac{X_i}{p}\right)^b, \tag{10}$$

where a and b are constants depending on the gas and were determined from two points which fell exactly on the curve. This gave the following equations for the curves of Fig. 14 for hydrogen, carbon dioxide, and air respectively.

$$\begin{aligned} \frac{\alpha}{p} &= .0002667\left(\frac{X}{p} - 200\right)^{1.615}, \\ \frac{\alpha}{p} &= .0004029\left(\frac{X}{p} - 356\right)^{1.515}, \\ \frac{\alpha}{p} &= .0001594\left(\frac{X}{p} - 400\right)^{1.615}. \end{aligned} \tag{11}$$

From equation (10)

$$\alpha = ap\left(\frac{X}{p} - \frac{X_i}{p}\right)^b.$$

Substituting this value of α in the equation $n = n_0 e^{\alpha d}$ and taking the logarithm of both sides gives

$$\log_e \frac{n}{n_0} = apd\left(\frac{X}{p} - \frac{X_i}{p}\right)^b. \tag{12}$$

This equation with the values of the constants a, b, and X_i/p given in equation (11) was applied to all of the data on pure gases.

The observed values of n/n_0 (see Tables I., II., III.) were substituted in equation (12) and the values of the field strengths X' computed which ought to give that current according to the theory. These computed values of X are given in the fourth column of Tables I., II., III., under the heading X' to distinguish them from the applied field strengths given in the first columns of the same tables under the heading X. The observed and computed values are in nearly all cases within the experimental error, the mean per cent. of difference between them for any gas being less than 1.5 per cent.

APPLICATION TO MIXTURES.

In the following discussion, if we have m per cent. of one gas present in a mixture and $(100 - m)$ per cent. of another gas, we mean by this that the partial pressure of the first is m per cent. of the total pressure of the mixture and that therefore m per cent. of the molecules present are of the first gas and $(100 - m)$ per cent. are molecules of the second gas.

Let Q_1 be the cross section of the first kind of molecules.

Let Q_2 be the cross section of the second kind of molecules.

Let L_1 and L_2 be the mean free paths of the pure gases respectively.

Let the total cross section Q_1 of the first pure gas be represented by 100. Then if we take a mixture of gases containing m per cent. of the first kind and $(100 - m)$ per cent. of the second kind, the total cross section Q_m of the mixture for the same pressure will be

$$Q_m = mQ_1 + (100 - m)Q_2$$

or

$$Q_m = mQ_1 + (100 - m)Q_1\frac{L_1}{L_2}, \tag{13}$$

since from the kinetic theory $Q_1/Q_2 = L_2/L_1$.

Then if the electron is negligibly small and moves with a velocity of order higher than that of the molecules, we may consider the molecules at rest and take the mean free path of the electron in the mixture to be inversely proportional to the cross section Q_m of the mixture. Then if l_1 is the mean free path of the electron in the pure gas and l_m in the mixture we have

$$\frac{l_1}{l_m} = \frac{Q_m}{Q_1}. \tag{14}$$

For hydrogen and air $L_H/L_A = 1.88$. If we let $Q_H = 100$ represent the total cross section of pure hydrogen, Q_{25}, Q_{50}, and Q_{75} represent the total cross sections of mixtures of hydrogen and air containing 25, 50, and 75 per cent. of air respectively, and Q_A the total cross section of air, all for the same pressure, we have, applying equation (13)

$$\begin{aligned} Q_H &= 100, \\ Q_{25} &= 75 + (25 \times 1.88) = 122, \\ Q_{50} &= 50 + (50 \times 1.88) = 144, \\ Q_{75} &= 25 + (75 \times 1.88) = 166, \\ Q_A &= 188. \end{aligned} \tag{15}$$

From the above it is evident that in a mixture of 75 per cent., hydrogen and 25 per cent. air, for example, the mean free path of the electron would be 1.22 times as small in the mixture as in the pure hydrogen at

the same pressure. Thus the mean free path of the electron in this mixture is the same as it would be in pure hydrogen at a pressure 1.22 times as great.

In general the electron will behave in ionizing the hydrogen in any mixture as though the pressures were Q_m/Q_H times p where Q_m is the cross section of all the molecules in any mixture and Q_H is the cross section that they would have were they all hydrogen molecules. This new value will be called the apparent pressure and will be denoted by P_1 or

$$P_1 = \frac{Q_m}{Q_H} p. \tag{16}$$

Similarly the electron will behave in ionizing the air in the mixture as though the pressure were

$$P_2 = \frac{Q_m}{Q_A} p. \tag{17}$$

Since there are m per cent. of the hydrogen molecules present at an apparent pressure P_1 and $(100 - m)$ per cent. of the air molecules at an

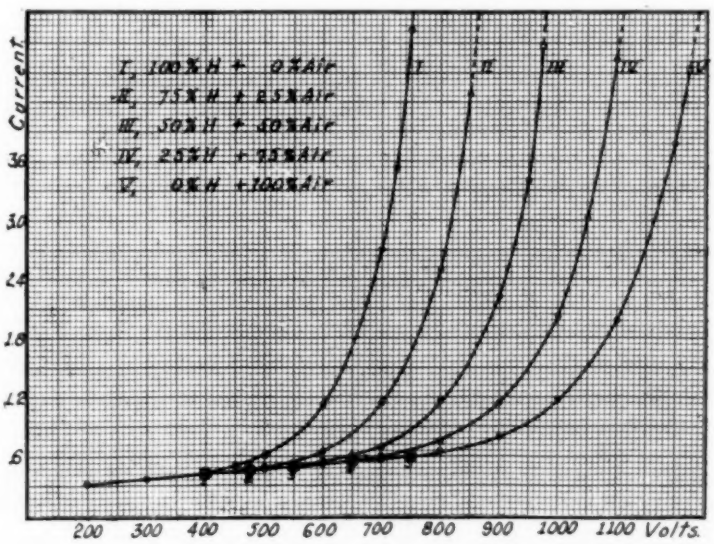

Fig. 15.

apparent pressure P_2, then equation (12) for a pure gas will become for a mixture of two gases

$$\log_e \frac{n}{n_0} = ma_1P_1d\left(\frac{X}{P_1} - \frac{X_{i_1}}{p}\right)^{b_1} + (100 - m)a_2P_2d\left(\frac{X}{P_2} - \frac{X_{i_2}}{p}\right)^{b_2}, \tag{18}$$

where the subscripts refer to the first and second gases respectively. In first term of the right-hand member of equation (18) represents the part of the current due to the ionization of the first gas and the second term that due to the second gas.

For the ionization curves for mixtures of air and hydrogen (See Fig. 15) equation (18) becomes for the different mixtures

$$\text{I. } \log_e \frac{n}{n_0} = .0002667 \times 5 \times .3875 \left(\frac{X}{5} - 200\right)^{1.615},$$

$$\text{II. } \log_e \frac{n}{n_0} = .75 \times .0002667 \times 6.1 \times .3875 \left(\frac{X}{6.1} - 200\right)^{1.615},$$

$$+ .25 \times .0001594 \times 3.245 \times .3875 \left(\frac{X}{3.245} - 400\right)^{1.615},$$

$$\text{III. } \log_e \frac{n}{n_0} = .50 \times .0002667 \times 7.2 \times .3875 \left(\frac{X}{7.2} - 200\right)^{1.615},$$

$$+ .50 \times .0001594 \times 3.83 \times .3875 \left(\frac{X}{3.83} - 400\right)^{1.615}, \qquad (19)$$

$$\text{IV. } \log_e \frac{n}{n_0} = .25 \times .0002667 \times 8.3 \times .3875 \left(\frac{X}{8.3} - 200\right)^{1.615},$$

$$+ .75 \times .0001594 \times 4.415 \times .3875 \left(\frac{X}{4.415} - 400\right)^{1.615},$$

$$\text{V. } \log_e \frac{n}{n_0} = .0001594 \times 5 \times .3875 \left(\frac{X}{5} - 400\right)^{1.615}.$$

To apply the formulæ of (19) the values of the field strengths X' given in the third column of Table VIII. were substituted in the equations and there resulted the values of n/n_0 given in the second column of that table. From the curves (Fig. 15) it was possible to determine what experimental value of X would be required to give the same value of n/n_0, *i. e.*, the same ionization current. These experimental values are given in the first column of Table VIII. headed X. The actual pressure in these mixtures was 5 cm. and the distance between the plates A and B in all cases was .3875 cm. The agreement between the experimental values X and the computed values X' of the field strengths required to produce a given current in the mixtures in all cases was within the experimental error.

It will be noticed that the curves on mixtures of air and hydrogen, II., III., and IV., Fig. 15, are spaced between the curves for the pure gases, I. and V., almost proportionately to the percentage of the mixture. This

is what might have been expected since the ionizing energy for air is only six per cent. more than that for hydrogen, so that in mixing the two gases the main effect was to decrease the mean free path of the electron as we increase the content of the air in the mixture, thus increasing the field strength required to produce a given ionization current in approximately the same proportion that the mean free path of the electron has been decreased. The above proportion would be exactly true were the ionizing energies for air and hydrogen the same.

TABLE VIII.

Mixtures of Air and Hydrogen.

I. 100 % H, $n_0 = .420$.			IV. 25 % H, 75 % Air, $n_0 = .548$.		
X	n/n_0	X'	X	n/n_0	X'
1,128	1.15	1,161	1,735	1.03	1,807
1,290	1.44	1,290	2,034	1.34	2,064
1,564	2.77	1,548	2,334	2.13	2,323
1,817	6.68	1,807	2,600	3.92	2,581
1,858	8.18	1,871	2,716	5.57	2,710
1,923	11.10	1,935	2,830	8.16	2,839
II. 75 % H, 25 % Air, $n_0 = .458$.			V. 100 % Air, $n_0 = .600$.		
1,388	1.16	1,419	2,000	1.02	2,064
1,548	1.42	1,548	2,307	1.30	2,323
1,688	1.85	1,677	2,581	1.95	2,581
1,814	2.53	1,807	2,848	3.35	2,839
1,941	3.64	1,935	3,107	6.46	3,097
2,070	5.46	2,064	3,166	7.65	3,161
2,173	8.55	2,194			
III. 50 % H, 50 % Air, $n_0 = .496$.					
1,475	1.03	1,548			
1,798	1.39	1,807			
2,059	2.32	2,064			
2,335	4.60	2,323			
2,452	6.83	2,452			

Consequently it was thought desirable to further test the theory by using mixtures of gases which varied largely in their ionizing energies, and for this purpose mixtures of hydrogen and carbon dioxide were chosen, the ionizing energies of these gases being 1.58×10^{-11} ergs and 1.01×10^{-11} ergs respectively.

APPLICATION TO MIXTURES OF HYDROGEN AND CARBON DIOXIDE.

For hydrogen and carbon dioxide $L_H/L_{CO_2} = 2.83$. If we let $Q_H = 100$ represent the cross section of the hydrogen, Q_{25}, Q_{50}, Q_{75}, represent the

cross sections of mixtures of hydrogen and carbon dioxide containing 25, 50, and 75 per cent. of carbon dioxide respectively, and Q_{CO_2} the cross section of the carbon dioxide, then applying equation (13) we have

$$\begin{aligned} Q_{H} &= 100, \\ Q_{25} &= 75 + (25 \times 2.83) = 145.75, \\ Q_{50} &= 50 + (50 \times 2.83) = 191.5, \\ Q_{75} &= 25 + (75 \times 2.83) = 237.25, \\ Q_{CO_2} &= 283. \end{aligned} \tag{20}$$

If then we apply equations (16) and (17) to those in (20) we shall obtain the apparent pressures for each of the gases hydrogen and carbon dioxide in the mixture. Substituting these values of P_1 and P_2, the values of a_1, a_2, b_1, b_2, from equation (11), the values of m and $(100 - m)$ given in Fig. 16, the values of X_{i_1}/p and X_{i_2}/p for hydrogen and carbon dioxide respectively, and the value of d, all in the general equation (18) and we obtain the following five equations for the curves of Fig. 16.

$$\text{I.} \quad \log_e \frac{n}{n_0} = .0002667 \times 5 \times .4 \left(\frac{X}{5} - 200\right)^{1.615},$$

$$\text{II.} \quad \log_e \frac{n}{n_0} = .75 \times .0002667 \times 7.288 \times .4 \left(\frac{X}{7.288} - 200\right)^{1.615} + .25 \times .0004029 \times 2.575 \times .4 \left(\frac{X}{2.575} - 356\right)^{1.515},$$

$$\text{III.} \quad \log_e \frac{n}{n_0} = .50 \times .0002667 \times 9.575 \times .4 \left(\frac{X}{9.575} - 200\right)^{1.615} + .50 \times .0004029 \times 3.383 \times .4 \left(\frac{X}{3.383} - 356\right)^{1.515}, \tag{21}$$

$$\text{IV.} \quad \log_e \frac{n}{n_0} = .25 \times .0002667 \times 11.86 \times .4 \left(\frac{X}{11.86} - 200\right)^{1.615} + .75 \times .0004029 \times 4.192 \times .4 \left(\frac{X}{4.192} - 356\right)^{1.515},$$

$$\text{V.} \quad \log_e \frac{n}{n_0} = .0004029 \times 5 \times .4 \left(\frac{X}{5} - 356\right)^{1.515}.$$

The values of the field strengths given in the last column, Table IX., headed X' were then substituted in the equations of (21) and the corresponding values of n/n_0 computed. Then from the curves of Fig. 16 the experimental values of X which would give the same values of n/n_0 were determined and are given in the first column of Table IX., headed X.

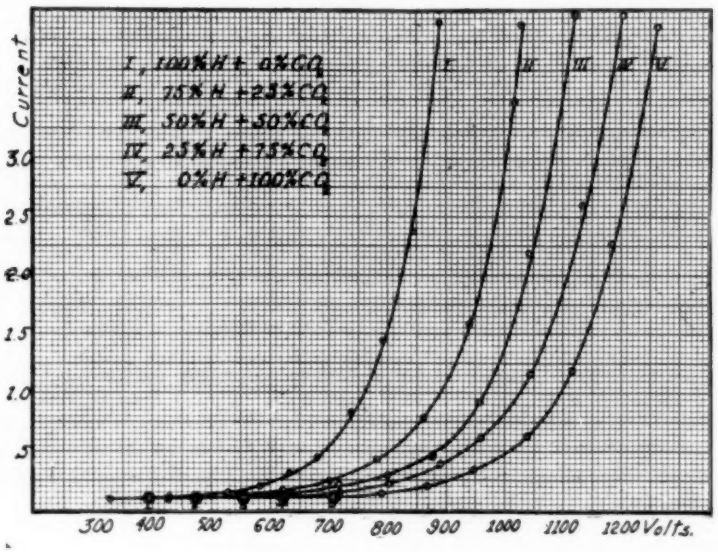

Fig. 16.

TABLE IX.

Mixtures of Hydrogen and Carbon Dioxide.

I. 100 % H, $n_0 = .095$.			III. 50 % H, 50 % CO_2, $n_0 = .099$.		
X	n/n_0	X'	X	n/n_0	X'
1,512	2.47	1,500	1,737	1.83	1,750
1,730	5.72	1,750	2,000	2.96	2,000
1,875	9.36	1,875	2,265	5.89	2,250
1,995	16	2,000	2,490	13.5	2,500
2,133	28.6	2,125	2,765	37.1	2,750
II 75 % H, 25 % CO_2, $n_0 = .097$.			IV. 25 % H, 75 % CO_2 $n_0 = .101$		
1,600	1.83	1,625	1,990	2.07	2,000
1,720	2.31	1,750	2,225	3.79	2,250
1,990	4.92	2,000	2,482	7.74	2,500
2,272	11.9	2,250	2,763	19.2	2,750
2,530	33.4	2,500	3,012	42.7	2,950

V. 100 % CO_2, $n_0 = .103$.

X	n/n_0	X'
2,225	2.20	2,250
2,487	4.49	2,500
2,763	10.5	2,750
3,043	28.0	3,000
3,140	38.6	3,075

The average per cent. of difference between the experimental values X and the computed values X' for the mixtures of hydrogen and carbon dioxide in Table IX. is .9 per cent.; for the mixtures of air and hydrogen in Table VIII. it is also .9 per cent., and for the pure gases, hydrogen, air, and carbon dioxide, in Tables VIII. and IX. it is .9 per cent., 1.5 per cent., and 1.1 per cent., respectively. From this it is seen that the theory has been checked with the same degree of accuracy in mixtures of gases as in pure gases, and that in practically all cases the computed and observed field strengths do not differ by more than the experimental error.

SUMMARY AND CONCLUSIONS.

1. The theory of ionization by collision has been verified for pressures as high as 40 centimeters.

2. The minimum ionizing energy for any gas is constant, being independent of the pressure and field strength so long as the latter is sufficiently high to produce new ions by collision.

3. These ionizing energies were here found to be 9.66, 6.21, and 10.21 volts, for hydrogen, carbon dioxide, and air, respectively.

4. The minimum ionizing field strength is directly proportional to the pressure, or $X_i/p = \text{cst}$, for pressures at least above one centimeter.

5. The relative ionizing energy of any two gases may be determined by

$$\frac{E_1}{E_2} = \frac{X_{i_1}}{X_{i_2}} \cdot \frac{L_1}{L_2}, \tag{1}$$

where E, X, and L are the ionizing energy, minimum ionizing field strength, and mean free path of the two gases. (2) Or by the second equation

$$\frac{E_1}{E_2} = \frac{V_1}{V_2},$$

where V_1 and V_2 are the potentials applied to plate A, when the pressures of the two gases are in the ratio

$$\frac{p_1}{p_2} = \frac{L_1}{L_2},$$

and n_0, α, l, and d are the same for both gases.

6. The general function

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$$

has been reduced to the special one

$$\frac{\alpha}{p} = a\left(\frac{X}{p} - \frac{X_i}{p}\right)^b.$$

This, combined with the equation $n = n_0 e^{ad}$ gives

$$\log_e \frac{n}{n_0} = apd\left(\frac{X}{p} - \frac{X_i}{p}\right)^b.$$

The second of these equations enables us to determine α for any field strength and pressure, and the third one enables us to compute the field strength required to produce a given value of n/n_0 for any pressure, and distance between plates, within the range of these experiments.

7. By combining the latter expression for two pure gases the value of n/n_0 for any field strength, pressure, and mixture can be computed by a formula of the general form

$$\log_e \frac{n}{n_0} = ma_1P_1d\left(\frac{X}{P_1} - \frac{X_{i_1}}{p}\right)^{b_1} + (100 - m)a_2P_2d\left(\frac{X}{P_2} - \frac{X_{i_2}}{p}\right)^{b_2}.$$

In conclusion the writer wishes to thank Professor Michelson and the staff of the Physics Department for their continued interest in this work, Mr. Fred Pearson for his kind assistance in setting up the apparatus, and especially Professor Millikan for suggesting the problem and for his valuable help and encouragement.

RYERSON PHYSICAL LABORATORY,
THE UNIVERSITY OF CHICAGO,
May 2, 1911.

STUDIES IN LUMINESCENCE.

BY EDW. L. NICHOLS AND ERNEST MERRITT.

XVI. THE FLUORESCENCE AND ABSORPTION OF CERTAIN URANYL SALTS.[1]

BECAUSE of their brilliant fluorescence and the interesting character of their absorption spectra the uranyl salts have frequently been the subject of study. The fluorescence spectrum consists of several narrow bands, as many as seven frequently being observable. At low temperatures the bands are so narrow as to be comparable with the bright lines of a gaseous spectrum. Upon observing the spectrum one is struck with the regular arrangement of the bands, which occur with increasing wave-length intervals in passing from violet to red. It would appear that there must be some connection between the bands analogous to that between the different lines of a spectrum series. The absorption spectra of the dissolved salts also consist of a number of sharp and regularly spaced absorption bands, and the absorption spectrum of the solid salts, although less frequently studied, has been found to be of the same general character. It was pointed out by E. Becquerel[2] that the absorption bands appear to form the continuation of the series of fluorescence bands, and in 1885 H. Becquerel[3] found that in the case of uranyl nitrate the two series of bands overlap, so that certain bands may appear either as absorption bands or as luminescence according to the conditions of observation. The same phenomenon has recently been observed with uranyl potassium sulphate at the temperature of liquid hydrogen by J. Becquerel and Onnes.[4]

Our chief purpose in taking up the study of the luminescence of the uranyl salts was to determine whether the different bands of the luminescence spectrum are to be regarded as independent bands, each with its own region of excitation, or whether, as seemed more probable, they form a connected series, such that the excitation of one necessarily involves the excitation of all. In connection with this inquiry we have been led to extend the investigation so as to include other questions connected with the luminescence of these salts, and in the present communication shall describe the results thus far obtained.

[1] A portion of the apparatus used in this investigation was purchased under a grant from the Carnegie institution.

[2] Mémoires de l'Académie des Sciences, Vol. 40, 1872.

[3] Comptes Rendus, 101, p. 1252, 1885.

[4] Leiden Communications, No. 110, 1909.

Wave-lengths and Relative Intensities of the Bands in the Luminescence Spectrum.

A list of the salts studied, which were obtained from Kahlbaum, is given in Table I. In each case the wave-length of the crest of each of

Table I.

Wave-length and Relative Intensity of the Fluorescence Bands.

Uranyl Acetate.		Uranyl Nitrate (Crystals).		Uranyl Nitrate (Anhydrous).		Uranyl Phosphate.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
4,719	1.1	4,708				4,850	
4,875	38.1	4,869	45.2	4,849	43.5	5,015	78.
5,085	100.	5,086	100.	5,071	100.	5,239	100.
5,321	62.1	5,329	50.	5,311	54.	5,483	39.7
5,583	24.3	5,585		5,569		5,748	
5,874	4.2	5,866		5,854			
		6,188		6,145			
Uranyl Sulphate.		**Uranyl-potassium Sulphate.**		**Uranyl Chloride.**[1]		**Uranyl Fluorid, Fluor Ammonium.**	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
4,757	2.3	4,766	1.8	4,769		4,843	5.1
4,925	38.	4,920	41.8	4,950		5,008	49.2
(4,891)							
5,149	100.	5,130	100.	5,121		5,237	100.
(5,097)							
5,397	58.8	5,360	65.1	5,369		5,460	57.2
(5,340)							
5,662	21.6	5,606	24.2	5,631		5,727	33.2
5,930	10.9	5,881	9.7	5,928		5,996	16.7
		6,190	2.0			6,294	

the fluorescence bands is also given. In measuring these wave-lengths a Hilger constant deviation spectrometer was used. This instrument was provided with two collimators, each having an adjustable slit, and with a Lummer-Brodhun cube; in fact, as constructed for our use it formed a Lummer-Brodhun spectrophotometer, similar in all respects to the usual instrument of this type except for the fact that a constant deviation prism was used. The calibation of the drum was frequently checked by reference to the mercury lines and found to be accurate to within one, or possibly two, Ångström units. The salt was excited by the rays from a quartz mercury lamp, the collimator slit being made as

[1] In the case of the chloride the fluorescence was so faint that no attempt was made to determine the relative intensity of the bands.

narrow as the brightness of the luminescence would permit. The crest of each band was located by means of the pointer in the eyepiece, this being set to the position of greatest brightness as estimated by the eye. Owing to the fact that the bands are so narrow no great error can be introduced by this procedure. Upon repeating the settings the different wave-length determinations rarely differed by more than two or three Ångström units, and the variation was usually less than this in the case of the brighter bands. We feel therefore that our wave-length determinations can scarcely be in error by more than five Ångström units and that the accuracy is probably considerably greater than this in the case of bright bands.

In all of the salts studied the general appearance of the luminescence spectrum was much the same, although the bands differed somewhat in width in the case of the different salts. The three principal bands of uranyl nitrate (crystals) are shown in Fig. 1,[1] the excitation being pro-

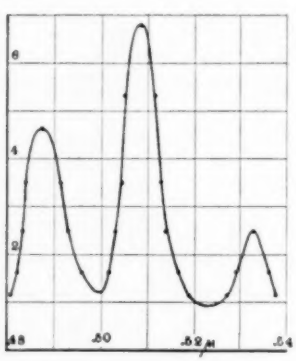

Fig. 1.

The three brightest bands of uranyl nitrate.

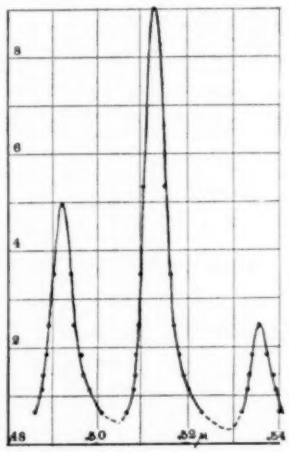

Fig. 2.

The three brightest bands of uranyl-potassium sulphate.

duced in this case by the violet line of the mercury arc at 0.43μ. In the double sulphate of uranyl and potassium (Fig. 2) the bands are much narrower as well as more intense.

The luminescence spectra of the different salts appeared to differ from one another chiefly as the result of a shift of the spectrum as a whole. In all cases the bands toward the violet end of the series, as well as those

[1] In Figs. 1 and 2 the ordinates show the intensities in the luminescence spectrum as compared with the intensities, for the same wave-lengths, in the spectrum of the acetylene flame.

lying toward the red, were relatively weak, and the bands of intermediate wave-length were the strongest. Upon measuring the intensities of the different bands in the case of the double sulphate of uranyl and potassium the relative intensities were found to be those indicated graphically in Curve *B*, Fig. 3. Each band is plotted as a line having the wave-length of the crest of the band, and the length of this line is proportional to the measured intensity. The intensity, which was first determined with reference to an acetylene flame, has been expressed in terms of energy,

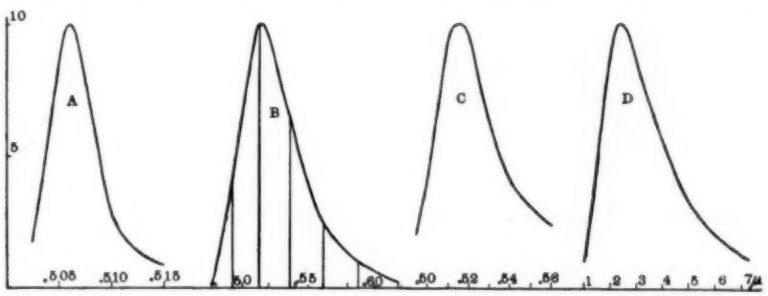

Fig. 3.

A. Energy distribution in the brightest fluorescence band of uranyl-potassium sulphate.

B. Distribution of energy among the seven fluorescence bands of uranyl-potassium sulphate.

C. Energy distribution in the fluorescence band of fluorescein.

D. Energy distribution in the spectrum of a black body at 1259°.

the curve of energy distribution in the acetylene spectrum determined in our previous work[1] being used for this purpose.

The distribution of energy among the different bands of the series in the case of the uranyl salts seems to be very similar to the distribution of energy in a single band of a luminescent substance like fluorescein, resorufin, or Sidot blende. To bring out this point we have sketched in a curve connecting the upper ends of the lines giving the intensity of the several bands, and for comparison the curve of energy distribution in fluorescein is plotted on the same diagram[2] (Curve *C*).

It is interesting to notice that the distribution of energy in a single band is very similar to the distribution among the several bands. To illustrate this we have plotted as Curve *A*, Fig. 3, the distribution in the brightest band of the double sulphate, the scale of wave-lengths being large as so to make the width of the single band as plotted approximately the same as the width of the groups of bands, *B*. In the same figure we have also plotted for comparison the curve of energy distribution for a

[1] PHYSICAL REVIEW, Vol. XXX., p. 328, 1910.

[2] See Nichols and Merritt, PHYSICAL REVIEW, Vol. XXX., p. 328, 1910.

black body at 1259° (Curve *D*) the wave-length scale in this case being greatly reduced.[1] It will be noticed that all four curves in Fig. 3 are obviously of the same type.

It is known that the width of each of the uranyl bands depends upon the temperature, these bands being almost as narrow as lines at the temperature of liquid air and reaching a width of perhaps 100 Ångström

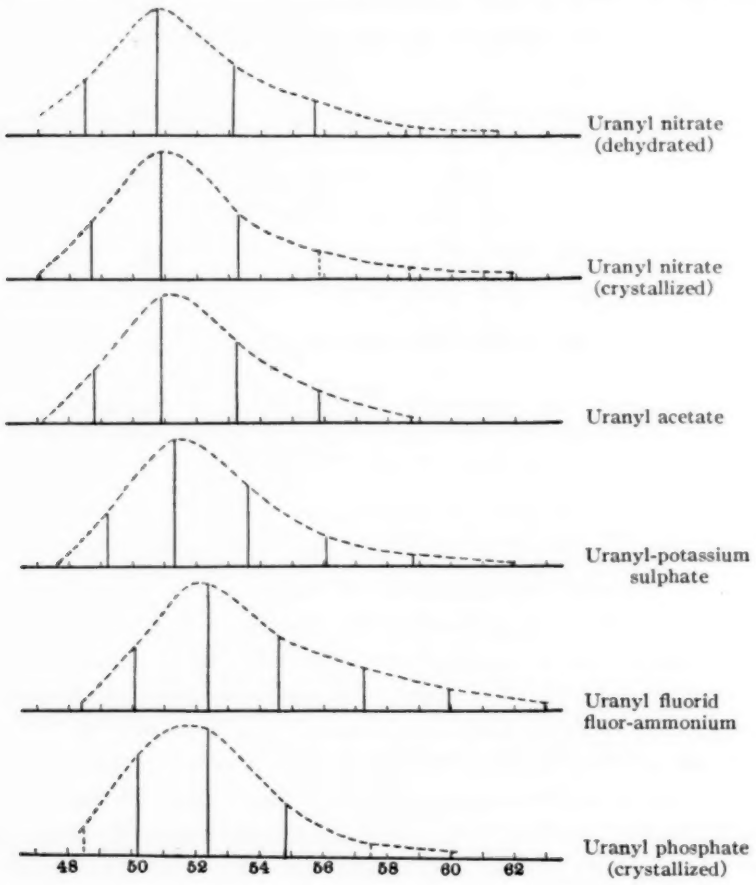

Fig. 4.

Relative intensity of the fluorescence bands of several uranyl salts.

units at ordinary temperatures. It seems probable that at still higher temperatures this broadening would continue and that finally the series of bands would overlap to such an extent as to appear as a single band having somewhat the shape of Curve *B* in Fig. 3. If observations were

[1] Plotted from the observations of Lummer and Pringsheim. See Kayser, Handbuch der Spectroscopie, Vol. 2, p. 120.

made at this high temperature only it would not be possible to distinguish the individual bands, and it would be natural to ascribe the luminescence to a single broad band. It appears to us not unlikely that in the case of many luminescent substances the conditions at ordinary temperatures are those which would probably obtain for the uranyl salts at high temperatures, and that the broad luminescence band of a substance like fluorescein is in reality the result of the overlapping of a series of bands. We have indeed recently presented experimental evidence of the complexity of this and other fluorescent compounds.[1]

The relative intensity of the different bands was determined in the case of several salts. The results are presented graphically in Fig. 4 and numerical values are given in Table I.[2] It is clear that the law of distribution of energy among the bands is much the same for all of the salts studied.

The shift in the wave-length of the bands as we pass from one salt to another does not appear to bear any simple relation to the molecular weight of the salt or of its acid component. If we compare, however, the anhydrous and the crystalline nitrate we find that there is a slight shift toward the longer waves in the case of the latter. This seems reasonable on account of the added weight of the water of crystallization.

Excitation by Light of Different Wave-lengths.

If all the bands of the luminescence spectrum are due to the vibrations of a single connected system it would be natural to expect that an agency which excited one would also excite the rest, especially if luminescence is due to the recombination of ions dissociated by the exciting light, or to the return of an electron set free by the exciting agency. On the other hand if each band is due to some process going on in one particular compound or molecular aggregation it would be natural to expect that wave-lengths might be found which would excite one band and not the rest, or which would at any rate excite the bands in different degree.

To test this matter we have measured the distribution of intensity in the bands for excitation by different lines in the ultraviolet spectrum of the quartz mercury lamp. The intensity of fluorescence with this excitation is not sufficient to permit the measurement of all the bands, so that the three brightest bands only have been measured. In Table II.

[1] Physical Review, XXXII., p. 38.

[2] In the case of the nitrate (crystals) and the phosphate the intensity was measured only for the three brightest bands, and the lengths of the dotted lines indicating the intensity of the other bands are estimated. In the case of the anhydrous nitrate the inten ity was measured for four bands, but the results for the band at 5,569 were so erratic as to throw doubt on the value of the intensity plotted for this band.

the intensities for excitation by the different lines in the mercury spectrum are given for five different uranyl salts. Curves showing the

TABLE II.

Relative Intensity of Excitation of the Three Brightest Bands by Five Different Lines in the Spectrum of the Mercury Arc.

	Wave-length of Exciting Light.	Intensity[1] of Luminescence at Crest of			Ratio *a*/*b*.	Ratio *c*/*b*.
		Band *a*, 4,920 A.U.	Band *b*, 5,130 A.U.	Band *c*, 5,360 A.U.		
Uranyl-potassium	.436μ	12.5	22.7	7.45	0.55	0.33
sulphate.	.407	12.6	26.4	8.45	0.48	0.32
Band *a*.....4,920	.366	10.5	23.2	6.65	0.45	0.29
b.....5,130	.313	16.25	22.9	8.27	0.71	0.36
c.....5,360	.254	8.83	13.9	4.25	0.64	0.31
Uranyl phosphate.	.436μ	10.0	10.2	3.07	0.98	0.30
	.407	6.04	6.06	1.90	1.00	0.31
Band *a*.....5,015	.366	9.7	9.7	2.47	1.00	0.25
b.....5,239	.313	11.1	10.4	3.04	1.07	0.29
c.....5,483	.254	6.85	5.35		1.28	——
Uranyl nitrate	.436μ	22.9	38.7	15.5	0.59	0.41
(anhydrous).	.407	15.3	22.7	9.30	.67	0.41
Band *a*.....4,849	.366	15.3	20.7	8.87	.74	0.43
b.....5,071	.313	21.8	31.6	11.7	.69	0.37
c.....5,311	.254	6.0	7.7	3.2	.78	0.42
Uranyl nitrate	.436μ	18.6	27.2	10.0	0.69	0.37
(crystals).	.407	17.5	24.5	8.6	0.73	0.35
Band *a*.....4,869	.366	12.2	18.3	7.5	0.67	0.41
b.....5,086	.313	17.3	25.6	9.6	0.67	0.38
c.....5,329	.254	8.3	10.5	4.0	0.79	0.38
Uranyl fluorid fluor-	.436μ	10.3	11.2	3.7	0.92	0.33
ammonium.	.407	23.3	25.0	7.7	0.93	0.37
Band *a*.....5,008	.366	20.4	25.7	7.6	0.79	0.30
b.....5,237	.313	37.5	43.4	11.5	0.87	0.27
c.....5,460	.254	15.8	17.6	5.7	0.90	0.32

variation of the relative intensity with the wave-length of the exciting light are shown for uranyl nitrate crystals in Fig. 5, and for the double sulphate in Fig 6. In each case the intensity of the most intense band has been put equal to 10. The variation was greater in the case of the double sulphate than in the case of any other salt studied. The observations were repeated in the case of this substance on two different days and a comparison of the full and dotted curves indicates the extent to which the results agree. In the case of the other salts studied curves very similar to that of Fig. 5 were obtained.

[1] The intensities given in Table II. are not corrected for the energy distribution in the acetylene flame.

It will be noticed that the lower curve in Figs. 5 and 6 indicates a very nearly constant ratio between the intensity of the brightest band and that of the band lying next in the direction of the red. But if we compare the brightest band with the band lying next on the violet side we find a

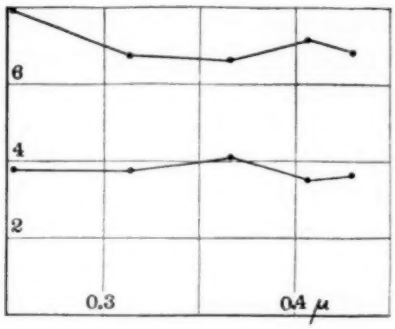

Fig. 5.

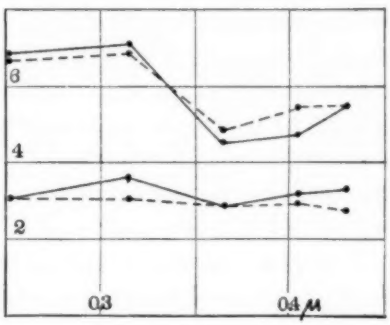

Fig. 6.

Showing the relative intensities of the brightest fluorescence bands of uranyl nitrate (Fig. 5) and uranyl-potassium sulphate (Fig. 6). The intensity of the brightest band is put equal to 10. The upper curve in each figure refers to the band lying next to the brightest toward the violet. The lower curve refers to the band toward the red. Abscissas give the wave-length of the exciting light. [See Table II.]

considerable variation in the ratio of intensities, especially in the case of the double sulphate. It appears to us probable that this variation is the result of a partial absorption of the luminescence by the substance. The absorbing power of a given salt is probably different for the different mercury lines used, so that in some cases the exciting light may penetrate much further into the substance than in others. It is clear that those bands for which the absorption is greatest will appear relatively weaker when the exciting light penetrates a considerable distance into the substance, even if the relative intensity of the excitation of the different bands is really the same for all wave-lengths of the exciting light. The observed distribution of energy would correspond with the actual distribution only in case an excessively thin layer of the substance is excited,—so thin that the absorption of the light emitted is negligible. As a matter of fact the band lying to the violet side of the maximum is in a region where the absorption is considerable; while the brightest band and those lying to the red are in the region where the absorption is small. The constancy of the ratio in the case of the lower curves, and the small variation of the ratio shown by the upper curves are therefore entirely consistent with the view that the observed variations are the result of absorption, and that the first effect of excitation, whatever may be the wave-length of the exciting light, is to produce all of the bands with a definite and constant intensity distribution.

Absorption of the Solid Salts at Ordinary Temperatures.

The salts studied by us were in powdered form, none of the crystals being large enough to use for the study of absorption by direct transmission. We have found it possible, however, to determine the location and approximately the relative intensity, of the different absorption bands by measuring with the spectrophotometer the intensity of the light transmitted through an extremely thin layer of the powder held between two plates of glass. Some idea of the character of the absorption spectrum of the salt can also be obtained by observing the spectrum of white light reflected from the surface of the powder, and this method was in some instances used.

The results of measurements of the intensity of the light transmitted by a thin layer of the double sulphate are plotted in Fig. 7, the source of

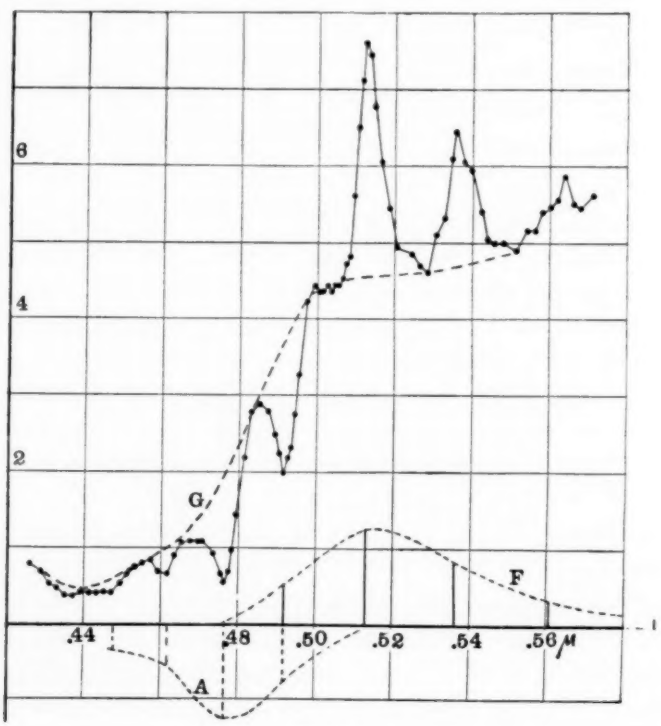

Fig. 7.

Transmission of a thin layer of uranyl-potassium sulphate, showing absorption bands and three of the fluorescence bands. Curves *F* and *A* show the relative intensities of the bands of fluorescence and absorption respectively.

light being an acetylene flame. The measurements cover not only a considerable portion of the absorbing region, but also a part of the region

containing the fluorescence bands. Three of these bands show very clearly, even when superposed upon the brilliant continuous spectrum of the acetylene flame. The absorption begins a little on the violet side of the brightest luminescence band and extends to the edge of the visible spectrum. It will be noticed that there are several definite and narrow absorption bands, which appear to be superposed upon a broad band, or region, of general absorption. It is not impossible, however, that this appearance of a broad band results from the overlapping of the group of narrow absorption bands, and that only the crests of these can be observed. There does not appear to be any way of deciding which of these views is correct. In estimating the relative intensity of the absorption bands we have adopted the first view and have assumed a general absorption such as is indicated by the dotted line of Fig. 7. The deviations from this dotted curve have been ascribed to the effect of the narrow bands. The intensity of each band is determined by taking the ratio of the diminution of the transmission which it produces to the transmission which would be expected if the general absorption only were present.

Both the absorption bands and the fluorescence bands have been indicated in Fig. 7 by lines whose lengths are proportional to the intensities of the bands. If a line is drawn through the ends of the lines that give the intensity of the absorption bands a curve (A) is obtained which is very similar in form to the absorption curve for a substance like fluorescein. This curve also has the same position with reference to the envelope of the luminescence bands (F) that the absorption curve in fluorescein has to the luminescence curve. It appears highly probable that just as a broad luminescence band may result from the overlapping of a group of bands, so the absorption of the same substance may result from the overlapping of a similar group of absorption bands.[1]

The transmission curve for a thin layer of powdered uranyl sulphate is shown in Fig. 8, the source of light being an acetylene flame. In its general features this curve is similar to that for the double sulphate of uranyl and potassium. The fluorescence of the sulphate is not so brilliant and the fluorescence bands therefore show less prominently. The sulphate has the peculiarity of possessing two series of fluorescence bands lying close together, one set of bands being much more intense than the other. It will be noticed that the absorption bands are also double. If we think of the more intense luminescence bands as constituting the principal series and the less intense bands forming a second-

[1] If we are mistaken in assuming a broad band of general absorption, upon which narrow bands are superimposed, Curve A, Fig. 7, will be shifted to the left and will have its crest at 0.44μ instead of at 0.48μ. But its general form will remain the same.

ary series, a curious reversal is noticeable as we pass from the region of fluorescence to the region of absorption. Each band of the principal series in the luminescence region lies a little to the right of the corresponding band of the secondary series. The positions of the bands are indicated by short vertical lines in the lower part of Fig. 8, the bands of the secondary series being represented by dotted lines. When we pass to the absorption series, however, the more intense band lies to the left in each case. For example, the absorption band at 4,925 corresponds in position with a fluorescence band of the principal series; but the absorption band at 4,880, which probably corresponds to the band 4,890 of the secondary fluorescence series, is by far the more intense of the two.

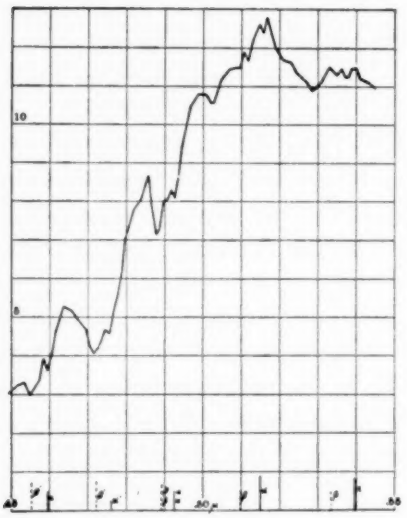

Fig. 8.

Transmission of a thin layer of uranyl sulphate.

It will be observed that the absorption bands of uranyl-potassium sulphate occurring at 4,760 and 4,920 (Fig. 7) appear to coincide in position with two of the luminescence bands of the same substance. In other words these two bands are "reversible" and may appear either as absorption bands or as luminescence bands according to the conditions under which they are observed. The double sulphate thus shows the same phenomenon that was first described by H. Becquerel[1] in 1885 in the case of uranyl nitrate.

The question whether the wave-length of the absorption band is exactly the same as that of the corresponding luminescence band, or whether the agreement is only approximate, is manifestly of great importance, and we have made a number of experiments to test this point. Special precautions were necessary, for when a luminescence band occurs in a region where there is appreciable absorption it is clear that the apparent position of the crest of the band may be influenced by absorption in case the latter is not uniform. Where measurements of absorption are made with light containing rays that are capable of exciting fluorescence there may also be a displacement of the crest of the absorption band owing to the presence of luminescence. There could be no displacement

[1] Comptes Rendus, Vol. 101, p. 1252, 1885.

of this sort in case the light emitted were strictly proportional to the coefficient of absorption; but if the fluorescence band and the absorption band do not exactly coincide in position or in form such a displacement is to be expected.

In order to avoid the necessity of changing the adjustment of the spectrophotometer, or the position of the substance, between measurements a thin layer of the double sulphate was in some cases mounted permanently in front of the slit. To locate the absorption bands the slit was illuminated, through the specimen, with light from an acetylene flame. To observe the luminescence bands a piece of blue glass was placed in front of the flame, so as to cut off the rays having the same wave-length as the bands while permitting the exciting rays to pass; or in some cases the acetylene flame was replaced by a mercury arc. To guard against the presence of fluorescence in measurements of absorption a green glass was sometimes used.

With the relatively thick specimen first used the absorption was so great that the band at 4,760 could not be observed. The band at 4,920 was well defined, however, and could be accurately located. If the eye-piece pointer was set at the crest of the absorption band and the source of light then changed so as to bring out the fluorescence band, the latter was seen to be very obviously displaced toward the red. Photographs of the absorption and fluorescence spectra taken on the same plate also showed the relative displacement of the two bands very clearly. The wave-length of the fluorescence band as measured under these conditions was not the same, however, as that previously determined, and the whole appearance of the band was different from what had been observed when looking at the front surface of the luminescent substance.

More definite conditions for observing the absorption band were obtained by using nearly monochromatic light for transmission measurements. The spectrum of a Nernst glower was formed by a large spectrometer and a small region of the spectrum was isolated by means of a suitable screen containing a slit. The light coming through this slit, after passing through the specimen to be studied, fell upon the slit of the spectrophotometer. By suitable adjustment the center of the band of transmitted light could be made practically coincident with the center of the absorption band and the latter could be located with considerable accuracy. Under these circumstances the transmitted light contained no rays capable of exciting any observable fluorescence, so that we may look upon the determinations of absorption by this method as uninfluenced by errors due to the presence of luminescence.

Using a relatively thick layer the absorption band was located at

4,919, while the crest of the fluorescence band (observed by transmission) lay at 4,974. An excessively thin layer, formed by depositing the salt from a solution, or suspension, in alcohol, gave a fluorescence band whose crest was at 4,925, while the wave-length of the very faint absorption band was 4,922. Our previous determination of the wave-length of the luminescence band, when looking at the surface exposed to the exciting rays, was 4,920. These results appear to us to warrant the conclusion that if disturbances due to absorption could be entirely eliminated the two bands would be found to have exactly the same wave-length.

It must not be forgotten however that it is nearly impossible to observe the fluorescence spectrum under conditions which entirely eliminate effects due to absorption. The exciting light always penetrates to some extent beneath the surface, so that some of the emitted light must pass through the fluorescent material before it can reach the eye. It is natural, therefore, to expect a slight displacement in all cases. Although our most reliable measurement of the wave-length of the absorption band, 4,919, and our best determination of the crest of the luminescence band, 4,920, differ by less than the probable errors of measurement, we feel that it is not unlikely that the difference is a real one, due to the cause just cited.

The absorption band at 4,760 in the double sulphate differs in position by 5 units from the fluorescence band at 4,765. A portion of this difference may also be explained by absorption. But it is probably chiefly due to the difficulty in accurately locating the crests of these bands. The fluorescence band is extremely faint, while the absorption band is not very sharp because of the large general absorption in this region.

Using a thick layer, formed by grinding down a translucent mass of adhering crystals until a piece about 0.5 mm. thick was obtained, a faint absorption band was observed at 5,127. This corresponds to the brilliant fluorescence band at 5,130. In all likelihood the coincidence here is complete, since measurements of the fluorescence band made at the same time and with the same specimen as that used for absorption measurements gave the same wave-length, 5,127, for both bands.

EXCITATION BY LIGHT CORRESPONDING TO DIFFERENT PARTS OF THE ABSORPTION REGION.

It seemed a matter of some interest to determine the relative effectiveness of light of different wave-lengths in producing fluorescence, and experiments having this end in view have been made in the case of the double sulphate. We were particularly interested in determining whether wave-lengths falling within the sharp absorption bands at 4,918, 4,760, 4,615, etc., were especially effective in exciting luminescence.

The source of the exciting light used in these experiments was a Nernst glower which was mounted in place of the slit of a spectrometer. The spectrum was focused upon an opaque screen containing a narrow slit, and the light passing through this slit was used in exciting the specimen tested. The fluorescence spectrum was observed in a spectrophotometer, the specimen being set up at an angle of approximately 45° with the path of the exciting light so that the collimator of the spectrophotometer could be pointed at the illuminated surface without interfering with the exciting light. Enough of the exciting rays were reflected into the spectrophotometer to enable the range of wave-lengths used in each case to be determined. The spectrophotometer was then set at the crest of the principal fluorescence band and the intensity measured by comparison with an acetylene standard. Observations of this sort were repeated throughout the absorbing region. The results are shown in Fig. 9. It will be noticed that the regions of strong excitation at 4,910 and 4,775 correspond very closely to the two absorption bands at 4,920 and 4,766. Some slight indication is also present of the other absorption bands. It is clear, however, that the ability to excite luminescence is not confined to rays falling within the narrow absorption bands, but extends to the region of general absorption lying between. It is not possible to determine the specific exciting power of different rays, as was done in the case of eosin and resorufin,[1] because of our ignorance of the absorbing power of the salt for different wave-lengths.[2] The results indicate, however, that the specific exciting power varies only slightly with the wave-length, as was found to be the case with resorufin and eosin.

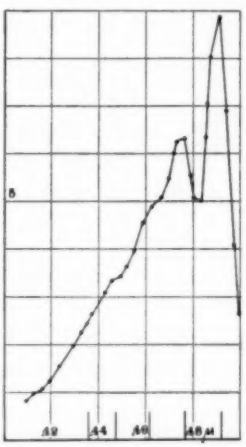

Fig. 9.

Intensity of fluorescence (ordinates) produced by exciting light of different wave-length (abscissas).

Fluorescence and Absorption at Low Temperatures.

To study the fluorescence spectrum at the temperature of liquid air the apparatus described in a previous article of this series[3] and shown in Fig. 10 was used. For excitation we found it preferable to use the undispersed light of a carbon arc. In studying absorption at low tem-

[1] Physical Review, XXXI., p. 381.

[2] The distribution of energy in the spectrum of the Nernst glower has also not been determined.

[3] Physical Review, XXXII., p. 38.

peratures the most convenient procedure was to reflect the light of an acetylene flame from the surface of the powder and compare the reflected light, by means of a spectrophotometer, with light received directly from a similar flame. A curve obtained in this way from the double

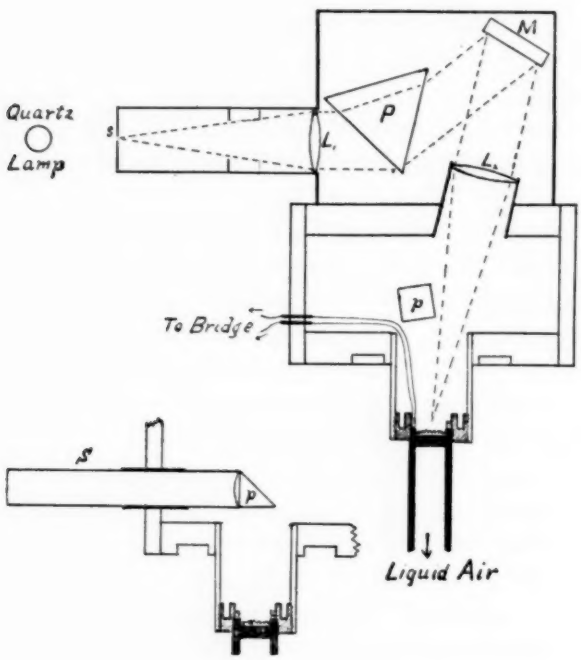

Fig. 10.

sulphate of uranyl and potassium is shown in Fig. 11. The region covered includes only two of the absorption bands. In the case of the dotted curve the light from the acetylene flame was first passed through a sheet of green glass, so as to largely remove the rays capable of exciting fluorescence. This was done in order to determine whether the shape and apparent position of the absorption band at 4,894 was influenced by the fluorescence in this region. No shift in the band due to this cause could be detected.

At low temperatures the fluorescence bands and the absorption bands appear to be much sharper than at ordinary temperatures. The narrowing of the fluorescence bands is undoubtedly a real effect, since it is verified by photographs of the spectrum and by spectrophotometric measurements. In the case of the absorption bands, however, we are in some doubt whether the narrowing is as great as it appears to be to the eye. If we compare Fig. 11 with Fig. 7, bearing in mind that the

horizontal scale is twice as great in Fig. 11 as in Fig. 7, it will be seen that the bands at the temperature of liquid air are not very much narrower than at ordinary temperatures. It must be remembered, however, that the comparison is not quite a fair one, since Fig. 7 is based upon observations of transmission and Fig. 11 on reflection. We do not have any curves that are entirely comparable. Photographs of the transmission spectra, however, at ordinary temperatures and at the temperatures of liquid air fail to show any very marked decrease in the width of the absorption band.

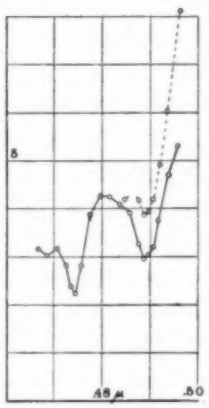

Fig. 11.

Reflection from uranyl-potassium sulphate at − 186° C.

There seems to be no great change in the "general" absorbing power in the violet region as we pass from ordinary temperatures to that of liquid air. To test this matter spectrophotometric measurements of transmission were made with a thin layer of the double sulphate, in powder form, throughout the absorbing region,[1] the measurements being made first at the temperature of the room and then after cooling with liquid air. The results are subject to some uncertainty on account of a slight deposit of frost, but indicate that the general absorption does not change by more than ten or fifteen per cent.

Both the fluorescence bands and the absorption bands show a slight shift in wave-length as the temperature is lowered. At the temperature of liquid air the fluorescence bands of the double sulphate are readily seen to be complex, as has already been pointed out by J. Becquerel. New fluorescence bands, and also new absorption bands, which are not in evidence at all at ordinary temperatures, also become easily observable at the low temperature. The results of determinations of the wave-length of such bands are given in Table V.

Relation between the Absorption and Luminescence Spectra.

In his important memoir on the phosphorescence of the uranium compounds[2] E. Becquerel pointed out in 1872 that the absorption spectrum of each of these substances, like the luminescence spectrum, consists of several regularly spaced narrow bands, and that these absorption bands appear to form a continuation of the series of emission bands in the luminescence spectrum. In 1885 H. Becquerel published wave-length

[1] The observations were made at such wide wave-length intervals that they are of no value in determining the effect of temperature upon the width of the sharp bands.

[2] Memoires del 'Academie des Sciences, Vol. 40, 1872.

measurements in the case of uranium nitrate,[1] indicating that the increment in wave frequency in passing from one band to the next is constant throughout the series, and that the suggestion of E. Becquerel that the absorption and emission bands belong to the same series is in agreement with the facts, since the frequency difference remains constant in passing from the luminescence to the absorption spectrum. H. Becquerel also showed that two of the bands were reversible; in other words, if the substances were exposed to suitable exciting rays these bands would appear as luminescence bands, whereas if light free from exciting rays was passing through the substance absorption bands would be found in exactly the same location. Reversible bands were also found by H. and J. Becquerel and H. K. Onnes when working with the double phosphate of uranyl and calcium at the temperature of liquid hydrogen.[2] Owing to the sharpness of the bands at this low temperature, and because of the fact that a grating was used, it is probable that the wave-length determinations were considerably more accurate in this work than in any that had preceded it. The photographs show that the absorption and luminescence bands are practically coincident, the difference of wave-length, if it exists, being a fraction of an Ångström unit.

TABLE III.

Absorption and Fluorescence Bands of Uranyl-Potassium Sulphate at Ordinary Temperature

Absorption.	Fluorescence.	$n\left(=\frac{3.10^{10}}{\lambda}\right)$	Δn
4,350		$6,896.4\times10^{10}$	
			188.1
4,472		6,708.3	
			206.3
4,614		6,502.0	
			206.1
4,760	4,765	6,295.9	
			198.4
4,920	4,920	6,097.5	
			249.5
5,127	5,130	5,848.0	
			251.0
	5,360	5,597.0	
			245.6
	5,606	5,351.4	
			250.2
	5,881	5,101.2	
			254.6
	6,190	4,846.6	

[1] Comptes Rendus, Vol. 101, p. 1252, 1885.

[2] Leiden Communications, No. 110, 1909.

In our own work with the double sulphate of uranyl and potassium we have confirmed the conclusions of H. Becquerel so far as the existence of reversible bands is concerned and have found in the case of this substance three such bands instead of two. We also find that the increments of wave frequency in passing from one luminescence band to another are very nearly constant. But this increment does not appear to have the same value for the absorption bands as for the luminescence bands, and there is thus a distinct break in the series in passing from luminescence to absorption. This fact is brought out in Table III., which gives the wave-lengths of the bands for uranyl potassium sulphate, together with the wave frequencies and the frequency differences. For the six luminescence bands beginning at 4,920 and ending at 6,190 the frequency differences are very nearly constant, the variation from constancy being not greater than the experimental errors. The series of absorption bands beginning at 4,350 and ending at 4,920 also shows a nearly constant frequency interval. But this differs so greatly from the interval between the luminescence bands that it is hard to believe that the two series of bands belong to the same spectral series.

TABLE IV.

Fluorescence Bands of Uranyl Sulphate and of Uranyl Acetate.

Sulphate.			Acetate.		
λ	Frequency $n = 3.10^{10} \div \lambda$.	Δn	λ	n	Δn
4,757	$6,306 \times 10^{10}$		4,719	6,357	
		215			203
4,925	6,091		4,875	6,154	
		265			254
5,149	5,826		*5,085*	5,900	
		267			262
5,397	5,559		5,321	5,638	
		261			265
5,662	5,298		5,583	5,373	
		239			266
5,930	5,059		5,874	5,107	

Our results with uranyl sulphate and uranyl acetate, Table IV., are similar in character to those obtained with the double salt. In the case of these salts, however, no absorption bands have been measured. It will be seen that the frequency interval is nearly constant throughout the series of luminescence bands, except between the first two, where the interval is much smaller. If these salts behave like the double sulphate the first three bands are reversible bands and the results are strictly analogous so far as they go to those obtained with the double sulphate.

Owing to the relative broadness of the bands at ordinary temperatures wave-length determinations at these temperatures cannot be very accurate. At lower temperatures, however, the bands become narrow and wave-lengths can be measured much more exactly. Our measurements of the wave-lengths in the case of the double sulphate of uranyl and potassium at the temperature of liquid air are therefore better suited to bring out any numerical relationships that may exist than the observations at ordinary temperatures. The low temperature measurements are given in Table V. As has been pointed out by Becquerel, each of the

TABLE V.

Absorption and Fluorescence Bands of Uranyl-Potassium Sulphate at $-186°$ *C.*

Absorption.	Fluorescence.	Frequency $n=3.10^{10}\div\lambda$	Δn_a	Fluorescence.	Frequency $n=3.10^{10}\div\lambda$	Δn_a
				(*a*) 5,114.7	$5,865\times10^{10}$	
(*a*) 4,323		$6,940\times10^{10}$		[5,114.8]		
4,437		6,761	221	(*b*) 5,135.5	5,842	
(*a*) 4,465		6,719				251
4,532.5		6,619		(*c*) 5,186.5	5,784	
4,590.5		6,535	196			
(*a*) 4,599.		6,523		(*a*) 5,343.5	5,614	
4,686.5		6,401	205	[5,342.4]		
(*a*) 4,748.5		6,318		(*b*) 5,366.5	5,590	
(*a*) 4,909.	4,907.	6,112	206			
	[4,904.2]			(*c*) 5,418.5	5,537	251
	(*b*) 4,929.5	6,086				
			247	(*a*) 5,593.5	5,363	
	(*c*) 4,974.5	6,031		[5,591.0]		
				(*b*) 5,614.5	5,343	
	(*a*) 5,114.7	5,865				246
	[5,114.8]			(*a*) [5,863.1]	[5,117]	
						239
				(*a*) [6,150]	[4,878]	

The wave-lengths enclosed in brackets are those measured by J. Becquerel and H. Kamerlingh Onnes (Leiden Communications, No. 110, 1909). The band at 6,150 was not observed by us but is recorded by H. Becquerel (Comptes Rendus, Vol. 144, p. 459, 1907).

bands is broken up at the temperature of liquid air into several very narrow bands. The wave-length of each of these has been measured. In several cases the same bands were located by Becquerel and Onnes and their values have also been included in the table. The most intense bands have been indicated by the letter *a*.

It will be noticed that the more intense bands form a series with practically constant wave-length interval. The variation from constancy is of importance only in the case of the interval between the last two bands

toward the red. One of these was measured by Becquerel and Onnes and the other by H. Becquerel 25 years earlier. Since both lines are faint, and since the apparatus used by H. Becquerel was not capable of great accuracy, it seems probable that the small value of the interval between these two bands is due to some error rather than to a real change in the law.

The five absorption bands which are most prominent also form a series with nearly constant frequency intervals. The absorption band of longest wave-length is a reversible band and corresponds almost exactly in position to the luminescence band of shortest wave-length. There is no reason to suspect that the difference in wave-length of two Ångström units which observations show is anything more than an accidental error.

At the temperature of liquid air we observed only one reversible band, and the luminescence band which at ordinary temperatures was observed at 4,757 was either not present or so faint as to escape observation. The band at 5,114, which is reversible at ordinary temperatures, is in all likelihood reversible at low temperatures. It is necessary at ordinary temperatures to use an especially thick layer of the substance to bring out this extremely faint absorption band and there is no reason to doubt that with proper conditions this band might have been reversed also at low temperatures.

In addition to the principal series, marked (*a*) in the table, there appear to be two other series, whose bands have been marked (*b*) and (*c*) respectively, in which the frequency intervals are also constant. These bands are fainter, however, and only a few can be observed in each series.

While our observations indicate that the frequency intervals between bands are constant within experimental errors, the measurements of Becquerel and Onnes in the case of uranyl salts at low temperatures show a slight tendency for the frequency interval to be smaller at the red end of the series. Although the variation is very slight it is observable in all of the cases studied by them, so that unless some unsuspected systematic error was present it seems that we cannot regard the law of constant frequency increments as being more than a close approximation.

It will be seen that all of our results indicate a distinct break in the spacing of the bands as we pass from the luminescence to the absorption region and thus do not agree with the results of H. Becquerel with uranyl nitrate. It seems to us not unlikely that the measurements upon which Becquerel's conclusions were based were in error. While we have ourselves made no measurements on the absorption spectrum of the nitrate, a large number of absorption bands have been determined for

this substance by Jones and Strong[1] and their measurements are not in agreement with those of H. Becquerel. In Table VI. we give the absorp-

TABLE VI.

Absorption and Fluorescence Bands of Uranyl Nitrate (cryst.) at Ordinary Temperatures.

Absorption Bands.	Fluorescence Bands.	Frequency $n = 3.10^{10} \div \lambda$.	Δn
3,600		$8,333 \times 10^{10}$	
			269
(3,720?)		8,064	
			231
3,830		7,833	
			210
3,935		7,623	
			216
4,050		7,407	
			213
4,170		7,194	
			177
4,275		7,017	
			207
4,405 [4,370]		6,810	
			217
4,550 [4,530]		6,593	
			221
4,705 [4,700]	4,708 [4,700]	6,372	
			211
4,870 [4,865]	4,869 [4,865]	6,161	
			263
	5,086 [5,080]	5,898	
			268
	5,329 [5,235][2]	5,630	
			259
	5,585 [5,583]	5,371	
			257
	5,866 [5,860]	5,114	
			266
	6,188 [6,180]	4,848	
			264
	[6,544]	4,584	

In this table the wave-lengths of the absorption bands are those determined by Jones and Strong (American Chemical Journal, Jan., 1910, p. 62).

The wave-lengths enclosed in brackets are those measured by H. Becquerel (Comptes Rendus, 101, p. 1252, 1885).

The wave-lengths of the fluorescence bands are based upon our own measurements.

tion bands as measured by Jones and Strong and the fluorescence bands as measured by ourselves. We have included also the values given by Becquerel in those cases where has he made measurements. In the case of the luminescence bands our wave-length determinations differ from those of Becquerel by more than possible experimental errors in only a few instances. Our determinations are also in close agreement with those of Jones and Strong in the case of the two reversible bands; but the absorption bands at 4,405 and 4,550 (as measured by Jones and Strong) do not correspond at all closely with the bands at 4,370 and 4,530 recorded by Becquerel. If we use the values given by Jones and Strong we find a series of constant frequency intervals throughout the greater portion of the absorption spectrum, but this interval differs by 20 per cent. from the frequency interval that holds throughout the luminescence spectrum.

[1] American Chemical Journal, Vol. XLII., Jan., 1910.

[2] This appears to be misprint for 5,325.

Effect of Water of Crystallization. Behavior of Solutions of the Uranyl Salts.

The study of the effect of water of crystallization upon the luminescence and absorption spectra of the uranyl salts, and the comparison of the spectra of the solid compounds with those of their solutions, offer an attractive and important field for further study. Since questions of this kind were aside from the chief purpose of the present investigation we have not gone into them at any length. A few points which have been brought out in the course of our work should, however, be recorded.

The effect of water of crystallization in the case of uranyl nitrate is to shift the luminescence bands slightly in the direction of the longer waves. (See Fig. 4 and Table I.) This is the effect which it would seem most natural to expect, since the mass of the vibrating system is increased by the addition of water of crystallization without any increase,

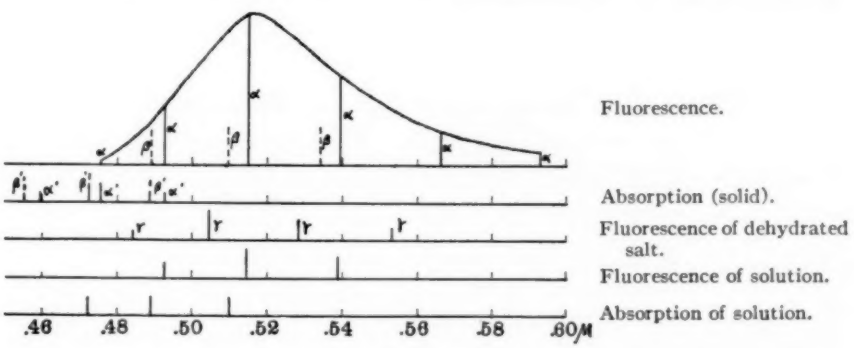

Fig. 12.

Showing the position of the fluorescence and absorption bands of uranyl sulphate.

so far as we know, in the elastic forces of the system. In fact the presence of water so intimately associated with the salt molecule would probably increase the effective dielectric constant of the region in which the vibrations occur, and would thus cause a decrease in frequency quite independent of any effect due to increase in mass.

It has been shown by Deusen[1] and by Jones and Strong[2] that the absorption spectrum of the crystallized nitrate is nearly coincident with the absorption spectrum of the aqueous solution. In many cases no difference can be detected in the wave-length of the band in solution and in the solid crystal. In the case of other bands, however, the difference appears to be too great to be accidental. It seems not unlikely that the

[1] Annalen der Physik, 43, p. 1128, 1898.

[2] American Chemical Journal, Vol. XLIII., p. 37, 1910. See also Vogel, Spectralanalyse, p. 270, 1889.

absorption spectrum contains several series of bands, some of which occupy almost identically the same positions for the solution as for the solid salt. We must assume therefore that at least a part of the dissolved salt has the same molecular structure as the solid crystals.

In the case of the uranyl sulphate studied by us the phenomena are more complicated. The luminescence spectrum of this salt, even at ordinary temperatures, contains two series of bands, which for convenience we shall designate the α and β series respectively. The α bands are by far the stronger and six of these could be observed. Of the relatively weak β bands only three could be seen. In the absorption spectrum of the solid salt two series of bands were also found (see Fig. 8) which we shall call the α' and β' bands. Two of the α' bands corresponded in position with two of the α bands of luminescence, while one band of the β' series corresponded with one of the β bands. The wave-lengths are given in Table VII. and are shown graphically in Fig. 12. It is a remark-

TABLE VII.

Uranyl Sulphate Fluorescence and Absorption Bands.

Fluorescence.	Crystals—Principal Series (α)	4763, 4929, *5148*, 5395, 5659, 5925.
	Crystals—Secondary Series (β)	4894, 5098, 5340.
	Dehydrated Salt (γ)	4843, *5049*, 5285, 5538.
	Concentrated Solution	4928, 5145, 5387.
Absorption.	Crystals—α' Series	4595, 4755, 4925.
	Crystals—β' Series	4555, 4720, 4880.
	Concentrated Solution	4718, 4887, 5095.

able fact that while the α bands are much the brighter in the luminescence spectrum, the α' bands in the absorption spectrum are much weaker than the β' bands.

The sulphate as received by us was in the form of small crystals. When the salt was dehydrated by being kept for about an hour in a stream of warm dry air its luminescence spectrum was found to be absolutely different, each band being shifted toward the violet by about 100 Ångström units. Brief exposure to the air apparently permitted a portion of the salt to return to the original condition, so that the original α and β bands could be seen as well as the γ bands characteristic of the dehydrated salt. In the case of a thin layer of the sulphate which had been dehydrated and then exposed for a short time to the air each of the luminescence bands was found to consist of three overlapping bands, the components corresponding in position to the α, β, and γ bands respectively Spectrophotometric measurements (with a rather wide slit) of the brightest luminescence band and of a portion of the absorption spectrum of the same layer are shown in Fig. 13. In the luminescence spectrum the β

bands are by far the most prominent,[1] while in the absorption spectrum the α' bands are strongest and no γ' bands can be detected. The results point to the existence of two different hydrated salts corresponding to

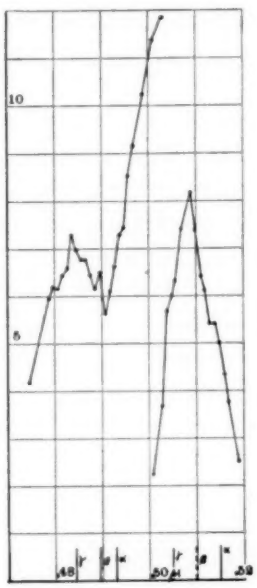

Fig. 13.

Uranyl sulphate (solid). Showing the brightest fluorescence band, at about 0.51μ, and a group of absorption bands, at about 0.49μ.

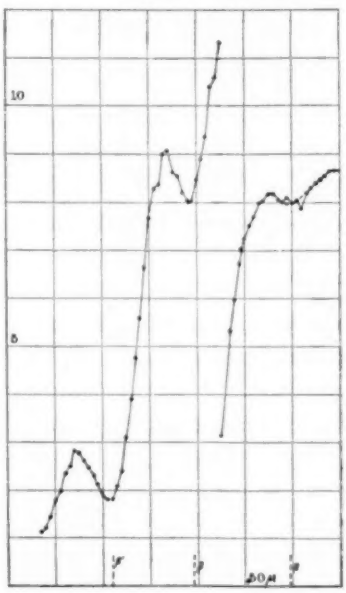

Fig. 14.

Uranyl sulphate (solution) showing at the left a portion of the transmission spectrum for a thin layer, and at the right for a thick layer.

the α and β bands respectively. But further study would be necessary to make possible an entirely satisfactory explanation of the observed phenomena.

The concentrated aqueous solution of the sulphate showed weak fluorescence, and the three brightest bands, which could be located with reasonable accuracy, were found to agree in position with three of the α bands of the solid crystallized salt. In the absorption spectrum of the concentrated solution it was possible to locate three well-defined bands, two of which corresponded with two of the β bands of the solid salt (see Fig. 14). The solution showed no trace of any fluorescence corresponding to the β series nor did it show any trace of absorption corresponding to the α' series. This peculiar behavior of the solution gives

[1] The α' band appears in Fig. 13 to be shifted by about 15 Ångström units toward the violet; whether this is a real shift, or whether it is due to disturbances due to simultaneous absorption and luminescence, we are unable to say.

support to the view that the absorption bands of the uranyl compounds do not belong to the same series as the luminescence bands, although they are undoubtedly similar in structure and intimately connected with the luminescence bands.

In a concentrated solution of uranyl-potassium sulphate (see Fig. 15) three absorption bands were found at 4,910, 4,730, and 4,570. These do

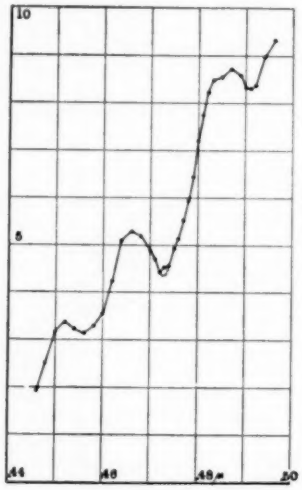

Fig. 15.

Transmission of a concentrated solution of uranyl-pottassium sulphate.

not agree in position with the corresponding bands of the solid salt, which occur at 4,920, 4,760, and 4,472. The solution of the double sulphate shows no trace of fluorescence.

DETERMINATION OF PELTIER ELECTROMOTIVE FORCE FOR SEVERAL METALS BY COMPENSATION METHODS.

By A. E. Caswell.

Introductory Note.—The great discrepancies between the values of the Peltier electromotive force between various metals obtained by different investigators, and especially between the values of Le Roux[1] and Jahn,[2] suggested the advisability of devising a new method of measurement not open to the objections which may be brought against the methods previously employed, and by such method redetermining the Peltier electromotive force for a number of combinations. The development of the thermo-electric and electron theories renders trustworthy determinations of this quantity more important than heretofore. Accordingly, upon the suggestion of Professor Fernando Sanford, the present work was undertaken, and throughout the writer has profited by his timely advice and suggestions as well as that of other members of the department.

Historical Sketch.

Discovery.—Peltier[3] was the first to discover that if a current be sent across the junction of two dissimilar metals there will be either an evolution or absorption of heat at the junction, and if the direction of the current be reversed the effect is also reversed. In other words, the junction of two dissimilar metals is the seat of an electromotive force. Its magnitude cannot be measured directly, so one must resort to the expedient of determining the amount of heat associated with the passage of a given quantity of electricity across the junction, or else deduce its value from more or less doubtful considerations.

Thomson's Theorem.—Through an application of the dynamical theory of heat to thermo-electric phenomena Sir William Thomson (Lord Kelvin) came to the conclusion that, if P = Peltier E.M.F., E = thermo E.M.F., T = absolute temperature, then $P = T\frac{dE}{dT}$.[4] The same considerations led him to the conclusion that a similar effect should

[1] Le Roux, Ann. Chim. Phys., IV., 10, pp. 201–291, 1867.

[2] Jahn, Pogg. Ann., N. F., 34, pp. 755–785, 1888.

[3] Peltier, Ann. Chim. Phys., II., 56, pp. 371–386, 1834.

[4] Kelvin, Lord, Math. and Phys. Papers, pp. 232–291, 1882; also Trans. Roy. Soc. Edinburgh, 1854.

exist between unequally heated portions of the same metal. The latter phenomenon was afterward discovered and is known as the Thomson effect. This discovery would seem to verify Thomson's conclusions. If we accept this equation two results follow: (1) knowing the way in in which the thermo E.M.F. varies at any temperature or its value for a very small range of temperature including the desired temperature, we may compute the value of the Peltier E.M.F. for that temperature; and (2) the value of the Peltier E.M.F. at the neutral temperature must be zero. From (1) it follows that at any given temperature the ratio of the Peltier E.M.F. to the thermo E.M.F. for any two metals should be constant and equal to the temperature (absolute). This point has been tested by most experimenters on the Peltier E.M.F. but the results in a number of cases have only been given in relative units. The second result has also been investigated. All the results of experiment seem to justify this equation in a general way.

Direct Determinations.—The direct determination of the amount of heat associated with the passage of a known quantity of electricity across a metallic junction was carried out by Le Roux who worked with copper against several other metals, notably bismuth. Bismuth bars were welded together into the form of a horse-shoe and to the ends heavy strips of copper were soldered. The junctions were immersed in rather crude calorimeters containing water. Current was sent for fifteen minutes in each direction and corresponding temperature changes in each calorimeter observed by means of mercury thermometers. In the copper-bismuth case the Joule heat was about four times the Peltier heat.

Edlund[1] obtained relative values for the Peltier E.M.F. by means of junctions inclosed in two nickel-plated copper tubes forming the two bulbs of a differential air thermometer. For comparison he also measured the thermo E.M.F. The electromotive force was determined by a sensitive galvanometer and the temperatures by two sensitive mercury thermometers. Assuming that his results for aluminium are the same as those which I have obtained I have computed his values of the Peltier E.M.F. and of the thermo E.M.F. These values are given in the following table. They probably do not differ from his true values by more than ten per cent. The computed values are expressed in millivolts.

Sundell,[2] working with Edlund's apparatus made similar measurements on antimony-bismuth alloys against copper, also on the bismuth used by Edlund. His value for copper-bismuth differed from that obtained by Edlund. This he attributed to some change in the crystalline structure of the bismuth.

[1] Edlund, Pogg. Ann., *143*, pp. 404–428, and 534–568, 1871; also *140*, pp. 435–450, 1870.
[2] Sundell, Pogg. Ann., *149*, pp. 144–170, 1873.

Jahn determined the Peltier heat by immersing one junction of a couple in a Bunsen ice calorimeter. Current was sent in both directions and the corresponding quantities of heat determined. From these measurements the Peltier heat was calculated. Jahn's results refer to 0° C., and apparently are accurate to within two or three per cent. In order to test the truth of Thomson's theorem Klemenčič measured the thermo E.M.F. of the couples used by Jahn. His results, multiplied by 273, the absolute temperature of Jahn's experiments, together with those of Jahn are shown in Table IX.

TABLE I.

Edlund's Probable Values.

Metal Used Against Copper.	Peltier E.M.F.		Thermo E.M.F. × 289.	
	Relative.	Computed.	Relative.	Computed.
—				
Iron	130.99	2.96	146.18	3.08
Cadmium	6.88	.155	9.79	.206
Zinc	.34	.008	.76	.016
Copper	——	——	——	——
Silver	1.29	.029	1.89	.040
Gold	14.76	.334	23.92	.505
Lead	22.20	.502	27.27	.575
Tin	24.71	.558	38.84	.82
Aluminium	30.77	.695	42.15	.89
Platinum	45.03	1.017	58.41	1.23
Palladium	96.23	2.175	115.04	2.43
Bismuth	783.1	17.70	835.1	17.62
+				

Cermak,[1] using Lecher's[2] thermo-electric calorimeter, has measured the Peltier effect for couples of constantan against iron, lead, tin, cadmium and mercury, and for a copper-nickel couple, over wide ranges of temperature. His results for the copper-nickel couple are as follows:

Temperatures	19	95	235	290	340	445
Gram-calories × 10^3	1.92	2.15	2.45	2.06	1.01	2.38

The result for 19° C. gives $P = 8.04$ millivolts. He has also found that there is no change either of the Peltier E.M.F. or thermo E.M.F. as the metals change from the solid to the liquid state, or vice versa.

Barker,[3] using the first of the methods employed in the present investigation which he independently devised, has measured the Peltier E.M.F.

[1] Cermak, Ann. d. Physik, *24*, 2, pp. 351–356, 1907; also *26*, 3, pp. 521–531, 1908. Also in Akad. Wiss. Wien, Sitz. Ber., 116, *2a*, pp. 657–668, 1907.

[2] Lecher, Wiener Ber., 115, *2a*, p. 1506, 1906.

[3] Barker, PHYS. REV., XXXI., p. 321, Oct., 1910.

for a copper-nickel couple and found it to be 6.75 millivolts at 28°.7 C.

The remainder of the work which has been done upon the subject is qualitative rather than quantitative. The values obtained are comparative and cannot be reduced to absolute units. The method used by Peltier himself was to solder two metals bars together in the form of a cross, connect two adjacent extremities to a galvanometer and the other two to a source of current. Current was then sent first in one direction for a given length of time and then in the opposite direction, and the corresponding changes in the galvanometer deflection noted. From these data one might arrange the metals in a Peltier series without giving the actual values of the E.M.F. between any pair. This method has been frequently used. Another common method is to make a thermo-electric couple of the pair of metals to be investigated, and arrange connections so that it may be quickly connected either to a source of current or a galvanometer. Current is sent through the couple thereby heating one junction and cooling the other. The circuit is then broken and the couple connected with the galvanometer. The galvanometer deflection may be used to compute the difference in temperature. For a given current this difference should be approximately proportional to the Peltier E.M.F.

Lenz[1] bored a small hole in the junction of two coaxial bars of bismuth and antimony. This he filled with water and cooled the whole apparatus to 0° C. Then by sending a current across the junction from bismuth to antimony he was able, not only to freeze the water in the hole, but also, to cool the ice to $-4°.5$ C.

Proportional to Current.—Icilius,[2] using a thermopile consisting of 32 bismuth-antimony couples, found that the heating or cooling of the junctions was proportional to the strength of the current sent across them. Frankenheim[3] confirmed this result by using Peltier crosses of bismuth-copper, copper-iron, bismuth-antimony, and iron-German-silver.

Zero at the Neutral Point.—Budde[4] investigated the question regarding the value of the Peltier effect at the thermo-electric neutral point for copper-iron and zinc-silver couples. In the latter case the thermo E.M.F. was too small for him to get any satisfactory results. Using the second of the qualitative methods mentioned above he found the Peltier effect to be zero at 240° C. and the thermo E.M.F. zero at 270° C. for the copper-iron couple. This he considered a sufficient agreement. In a

[1] Lenz, Pogg. Ann., *44*, p. 342, 1838.

[2] Icilius, Pogg. Ann., *89*, p. 377, 1853.

[3] Frankenheim, Pogg. Ann., *91*, p. 161, 1854.

[4] Budde, Pogg. Ann., *153*, pp. 343–372, 1874.

similar way Battelli[1] investigated the Peltier effect and thermo E.M.F. for lead against (1) an alloy of 10 parts antimony to 1 part tin, and (2) an alloy of 18 parts tin to 1 part cadmium. For the thermo E.M.F. he found the neutral points to be 12° C. and 16° C., respectively. The Peltier effect was zero at 16° C. and 31°.5 C. Believing that the experiments of Budde and Battelli by no means prove that the Peltier effect is zero at the neutral point, La Rosa[2] investigated the point very carefully. To the ends of a bar of pure zinc bent into the form of a V, he soldered iron and platinum wires. The iron wires were connected to the galvanometer, and current sent through the platinum-zinc junctions. Readings were taken from 19° C. to 46°.5 C., the neutral point being found at 36°.6 C. The curve for temperatures as abscissæ and galvanometer deflections as ordinates cut the temperature axis slightly above 36°.5 C. Therefore the Peltier effect becomes zero at the neutral point within the limits of experimental error.

Agreement with Thermo-electric Diagram.—Campbell,[3] using couples consisting of a U-shaped piece of lead or other metal soldered to iron blocks, obtained results which appear to agree with the thermo-electric diagram given in Tait's manual on "Heat." The temperature differences of his junctions were measured by means of an iron-German-silver thermo-couple, separated from the junctions by several thicknesses of paper. Gore[4] obtained similar results using a thermopile, consisting of 36 bismuth-antimony couples, heated in a hot-water jacketed chamber from 9° to 85° C. With Peltier crosses he also found that the Peltier effect increased with temperature for iron-German-silver, bismuth-antimony, and bismuth-silver. For antimony-silver it seemed constant.

Variation with Temperature.—By means of Thomson's equation, $P = T\frac{dE}{dT}$, Harrison[5] has found the value of the Peltier E.M.F. at the temperature of liquid air (− 191°.2 C.). His results are:

Copper-iron	1,156 microvolts.
Copper-nickel	7,697 microvolts.

Bausenwein[6] has found that, for the iron-constantan couple which he used, both the thermo E.M.F. and the Peltier E.M.F. increase in a

[1] Battelli, R. Acc. dei Lincei (1) Rendic., *3*, pp. 404–407, 1887, also Beibl., *11*, 726, 1887.

[2] LaRosa, Acc. Lincei, Atti, *13*, pp. 167–173, 1904; also Sc. Abs., *7*, 2968.

[3] Campbell, Proc. Roy. Soc. Edinburgh, *11*, 807, 1882–3; also Beibl., *8*, p. 231, 1884.

[4] Gore, Phil. Mag. 3, *21*, pp. 351–362, 1886.

[5] Harrison, Phil. Mag., 6, *3*, pp. 177–195, 1902.

[6] Bausenwein, Akad. Wiss. Wien, Sitz. Ber., *144*, *2a*, pp. 1625–1633, 1905; also Sc. Abs., *9*, 1110.

linear manner with the temperature (absolute). But the Peltier effect is not proportional to the absolute temperature, its curve cutting the axis of temperatures at $-600°$ C. Hence this combination does not obey Thomson's law. His experiments extended over the interval from 0° C. to 800° C. Rzika[1] carried out similar measurements on a couple made from the same metals and obtained contradictory results. The principal source of error is probably due to changes in the specific heats at high temperatures, which changes are not known. The question of variation with temperature is still unsettled.

Theories.—In addition to Sir William Thomson's theoretical work on thermo-electricity, two recent developments are of interest. The first is the explanation of the Peltier effect upon the basis of the electron theory,[2] the second is due to Lecher.[3]

Electron Theory.—In the electron theory it is assumed that the concentration of the electrons in any two metals is, in general, different for the same temperature. If, then, two metals are placed in contact, the electrons will diffuse from that metal in which the concentration is large to that in which it is small. This diffusion will continue until the electric field set up by the motion of the electrons away from their compensating positive charges is sufficient to balance the difference of pressure due to the difference of concentration. The resulting potential difference, assumed to be identical with the Peltier E.M.F., is given by the equation $P = \frac{4\alpha T}{3\epsilon} \log \frac{N_1}{N_2}$, where N_1, N_2 are the concentrations of the electrons in the two metals, αT is the mean kinetic energy of an electron, and ϵ is the charge on an electron. From other considerations N is found to be proportional to the inverse of the square root of the absolute temperature. Hence N_1/N_2 is constant. The Peltier E.M.F. should, therefore, be strictly proportional to the absolute temperature, and so could not be zero at the neutral point unless it were zero at all temperatures. This seems to be contrary to the facts.

Lecher's Diagram—Lecher obtains the Peltier heat by superimposing upon a diagram representing the Thomson heat for the two metals concerned, a curve representing the energy of the thermo E.M.F. between the two metals. In this way he finds the Peltier effect between iron and silver to be 7.3×10^{-4} gram-calories per coulomb, or 3.06 millivolts. This agrees well with experiment as may be seen by referring to Table IX.

[1] Rzika, Akad. Wiss. Wien, Sitz. Ber., *116*, 2a, pp. 715–722, 1907; also Science Abs., *11*, 26.

[2] Drude, Ann. d. Physik, 4, *1*, p. 566, 1900, and 4, *3*, p. 369, 1900.

[3] Lecher, Ann. d. Physik, 4, *20*, pp. 480–502, 1906.

Methods of Measurement.

Two methods of measurement were devised, both of which depend upon maintaining both junctions of the given couple at the same temperature by supplying heat at the junction where cooling is taking place. This precludes the possibility of error arising out of other thermo-electric effects. The Peltier electromotive force is determined by measuring the ratio of the heat so supplied to the quantity of electricity sent across the junction. The first method, as previously stated, has also been devised by Barker and by him employed in the measurement of the Peltier E.M.F. in a copper-nickel junction. In view of the fact that measurements were already being made by this method when his article was published, also that he had not investigated the method completely and intimated that he had discontinued the work, it was decided to proceed. The discussion of the method and the mathematical calculations here given are fuller than those in his article, and so may justify such repetitions as occur.

First, or Separate Heating-coil, Method.

This consists essentially in placing the two junctions of the couple in two separate calorimeters containing equal quantities of a suitable liquid. Each is provided with an electric heating-coil of known resistance, by means of which sufficient heat is supplied to the liquid where cooling is taking place to maintain it at the same temperature as that where heat is evolved, the equality of temperature being shown by a differential thermometer.

Two Dewar silvered glass vacuum flasks (inside dimensions: diameter 3.1 cm., depth 15 cm.) were used as calorimeters because they are the best heat insulators available and their heat capacity is small. These were held upright in a wooden box. The couples were made from heavy strips of the metals and were in the form of a double U, the junctions being at the bottoms of the U's.

Apparatus.—Three different forms of heating-coil were tried. The first coils, used only with the gas stirrers mentioned below, consisted of a considerable length of manganin wire doubled and then kinked as shown in Fig. 1. These were placed in the center of the U and extended upward to the surface of the liquid. This form was discarded because the coils occupied too much space. Coils of 65 cm. of German-silver resistance wire were then made. The wire was wound around a celluloid hoop, the perimeter of which was 6.5 cm. and depth 2.5 cm. The manner of winding is shown in Fig. 2. The hoop was placed in the

center of the U with its axis vertical, and the stirrer and one junction of the thermo-element, used as a thermometer, were placed within it. The resistance of these coils was 3.057 and 3.072 ohms, respectively. This arrangement was abandoned because the hoop, by impeding the circulation of the liquid, lengthened the time elapsing before a steady temperature condition could be set up. The arrangement finally adopted was similar to the first except that the wire was crowded into small space and placed in the bottom of the U as shown in Fig. 3. The length of

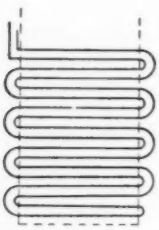

Fig. 1.

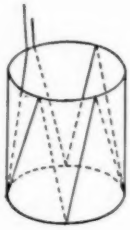

Fig. 2.

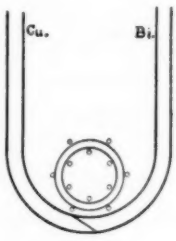

Fig. 3.

the coils so formed was 2.5 cm., so that they extended across the calorimeters. In this way heat was supplied very close to the place where it was being absorbed, and the coil, while being small, permitted free circulation of the liquid. Two sets were made in this way. They were of German-silver wire similar to that used in the "hoop" coils. The resistance of the first set was 4.503 and 4.509 ohms, and of the second set 1.490 and 1.505 ohms.

In the preliminary experiments instead of a differential thermometer two mercury thermometers, graduated to tenths of a degree Centigrade and readable to hundredths, were used. These were read as nearly simultaneously as possible. Owing to their comparatively great bulk, mercury thermometers are not suitable, and so were replaced as soon as possible by a differential thermometer consisting of four copper-constantan thermo-elements in series. No. 24 constantan and No. 26 copper wire were used. The resistance of the set was about 4.5 ohms. These were connected to a sensitive Siemens and Halske D'Arsonval galvanometer of 91.6 ohms resistance, the deflections being observed by means of a powerful reading telescope to which a glass scale was attached, the distance from mirror to scale being 150 cm. A deflection of 9.2 cm. corresponded to a temperature difference of 0°.1 C. The scale could be easily read to 0.01 cm. The sensitiveness of the apparatus varied to a certain extent because of the quantity of liquid not being always the same, and because the heat capacity of the immersed metal also differed for the different junctions. An idea of the sensitiveness may be gained

from the fact that in the case of the copper-silver junction (see section on copper-silver) a reversal of the heating effect of a current of 0.036 ampere through a coil of 4.5 ohms resistance produced a change of 0.27 cm. per minute in the rate of deflection of the galvanometer. That is, the addition of 2.59 joules of heat (0.62 calories) to one calorimeter would change the deflection of the galvanometer one centimeter. In the case of copper-platinum the addition of 2.18 joules was sufficient to change the deflection of the galvanometer one centimeter.

The stirring of the liquid was first attempted by means of gas stirrers. Each of these consisted simply of a capillary glass tube, one end of which was placed in the bottom of the calorimeter, the other being connected to a tank containing air under a slight pressure. These were used only with the mercury thermometers. It was found that whenever a bubble of air happened to strike the thermometer the latter tended to give the temperature of the air rather than that of the liquid, in consequence rotary stirrers were substituted in the later experiments. These consisted of semi-circular disks of copper, 0.4 cm. radius, soldered to steel knitting-needles. Each was supported and made adjustable by means of two bearings, one at the top of the calorimeter, the other about 7 cm. above it. The stirrers were driven by a small electric motor.

The openings of the calorimeters were partially closed either by cork stoppers, as in the case of copper-silver, or by pieces of cloth laid over the tops of the calorimeters. It was found that when the calorimeters were not shielded in any way the unequal lighting of the room had an appreciable effect upon the amount of heat required by each calorimeter, and in consequence the whole apparatus was surrounded by a box provided with a heating-coil, by means of which, with the aid of a thermostat, the air could be kept at a constant temperature. As will be seen later, it is not important that there should be no heat lost by the calorimeters, but that this loss should be as nearly as possible the same for both. This and other vitiating effects will be discussed under the head of probable sources of error.

Throughout the experiments kerosene was used as the calorimetric fluid, being chosen on account of its mobility and low specific heat. Equal amounts were measured into the calorimeters by means of a pipette. From 35 to 40 c.c. was used in each calorimeter.

In order to be able to determine the temperature difference of the metallic junctions during an experiment when the temperature of the liquid was the same in both calorimeters, they were connected to the galvanometer by means of a double-throw switch so that they could replace the thermo-elements. By determining their thermo E.M.F. by com-

parison, the temperature difference could be computed. This measurement must necessarily be made *after* the current through the junctions is stopped, and in consequence the deflection obtained is less than it should be owing to communication of heat to the liquid.

The approximate temperatures of the experiments were obtained by inserting a mercury thermometer into one of the calorimeters before and after a run and reading the temperature.

Currents were measured by means of Siemens and Halske milliammeters with suitable shunts. The compensating current was supplied by a single storage cell, while the main current was supplied by storage batteries of 4, 6, or 8 storage cells in series, or two sets of 8 cells in series in parallel, depending upon circumstances. The single cell supplied a perfectly uniform current, but the batteries frequently varied as much as one per cent., and occasionally as much as two or three per cent. These variations will not affect the final result materially since the current was read at regular intervals of one or two minutes each.

A sectional view of the calorimeters is shown in Fig. 4, while all the electrical connections are shown diagrammatically in Fig. 5.

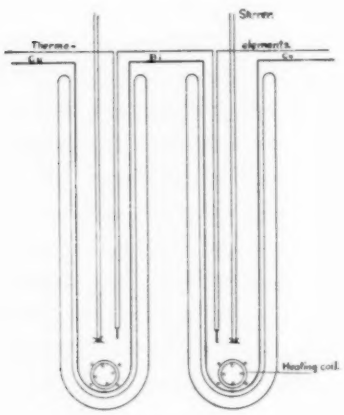

Fig. 4.

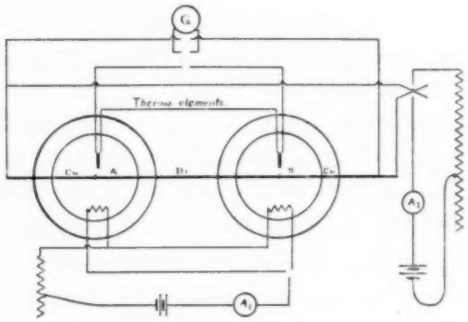

Fig. 5.

Mathematical Discussion.—The following mathematical discussion is somewhat more complete than that given by Barker, to which reference has already been made. If we denote the two calorimeters as A and B, and for the quantities corresponding to each use the subscripts a and b, respectively, we may use symbols for the quantities involved as follows:

P = Peltier E.M.F. expressed in volts,

r = resistance of compensating heating-coil in ohms,

R = effective resistance of junction,

i = compensating current in amperes,

I = main current through the junctions,
C = heat capacity of calorimeter and contents *expressed in joules*,
h = rate of heat loss to surrounding bodies dependent upon a difference in temperature of 1° Centigrade,
θ = temperature of liquid minus temperature of surrounding bodies,
s = heat gained from external sources independent of any temperature differences (*i. e.*, through stirring, etc.).

Case I.—When direction of the current is such that heat is absorbed in A, and evolved in B, we have

$$\frac{I_a^2R_a - PI_a + i_a^2r_a - h_a\theta_a + s_a}{C_a} = \frac{I_a^2R_b + PI_a - h_b\theta_a + s_b}{C_b},$$

or

$$C_a(I_a^2R_b + PI_a - h_b\theta_a + s_b) = C_b(I_a^2R_a - PI_a + i_a^2r_a - h_a\theta_a + s_a),$$

or

$$PI_a(C_a + C_b) = I_a^2(C_bR_a - C_aR_b) - \theta_a(C_bh_a - C_ah_b) + C_bi_a^2r_a + (C_bs_a - C_as_b),$$

whence

$$(1) \qquad P = \frac{I_a(C_bR_a - C_aR_b)}{(C_a + C_b)} + \frac{C_bi_a^2r_a}{I_a(C_a + C_b)} - \frac{\theta_a(C_bh_a - C_ah_b)}{I_a(C_a + C_b)} + \frac{C_bs_a - C_as_b}{I_a(C_a + C_b)}.$$

Case II.—In a similar way we may obtain the following equation for the case when the current is reversed.

$$(2) \qquad P = \frac{I_b(C_aR_b - C_bR_a)}{C_a + C_b} + \frac{C_ai_b^2r_b}{I_b(C_a + C_b)} - \frac{\theta_b(C_ah_b - C_bh_a)}{I_b(C_a + C_b)} + \frac{C_as_b - C_bs_a}{I_b(C_a + C_b)}.$$

Adding equations (1) and (2) we obtain

$$(3) \qquad P = \frac{1}{2}\left[\frac{I_a - I_b}{C_a + C_b}(C_bR_a - C_aR_b) + \frac{1}{C_a + C_b}\left(\frac{C_bi_a^2r_a}{I_a} + \frac{C_ai_b^2r_b}{I_b}\right) - \frac{\frac{\theta_a}{I_a} - \frac{\theta_b}{I_b}}{C_a + C_b}(C_bh_a - C_ah_b) - \frac{\frac{1}{I_a} - \frac{1}{I_b}}{C_a + C_b}(C_bs_a - C_as_b)\right].$$

If $I_a = I_b$, the first and fourth terms on the right-hand side of the equation vanish. This condition is easily realized. If, in addition, $C_a = C_b$, the second becomes $+\frac{i_a^2r_a + i_b^2r_b}{4I}$ and the third term becomes

$-\frac{\theta_a - \theta_b}{4I}(h_a - h_b)$. Since θ_a and θ_b are both small and approximately equal, the same being supposed to be true of h_a and h_b, the last term may be neglected without any great error. We have then simply

$$P = \frac{i_a^2 r_a + i_b^2 r_b}{4I}. \tag{4}$$

This equation is the one used in all the numerical computations. It depends as we have seen upon the assumption that $C_a = C_b$. This condition may not be very fully realized so it is advisable to consider equation (3) a little farther. Considering only the second and third terms, let us suppose that $C_a + c = C_b$, where c is small in comparison with C_a. Then

$$P = \frac{1}{2I(2C_a + c)}[C_a\{i_a^2 r_a + i_b^2 r_b - (\theta_a - \theta_b)(h_a - h_b)\} + c\{i_a^2 r_a - h_a(\theta_a - \theta_b)\}].$$

If we expand $\frac{1}{2C_a + c}$ by the binomial theorem and sum the resultant product as two geometrical progressions we obtain

$$P = \frac{1}{4I}[i_a^2 r_a + i_b^2 r_b - (\theta_a - \theta_b)(h_a - h_b) + \frac{c}{2C_a + c}\{i_a^2 r_a - i_b^2 r_b - (\theta_a - \theta_b)(h_a + h_b)\}]. \tag{5}$$

Obviously a small difference in the heat capacities of the calorimetric systems will have but little effect upon the final result, unless perchance h_a and h_b should be quite large, which is improbable.

Probable Advantages of Method.—Practically all the methods hitherto employed in the measurement of the Peltier E.M.F. involve temperature differences between the junctions which must necessarily involve both the Thomson and Seebeck effects. It is impossible to say with certainty what effect these phenomena will have upon the resulting value obtained for the Peltier E.M.F. These disturbing effects are effectually eliminated by the present method. This is shown by the temperature differences found for the junctions. Errors due to loss of heat to surrounding bodies, etc., are reduced to a minimum since the other methods used do not take account of it, and it must have been quite large in some cases. In other cases it is doubtful whether the temperature differences, or other quantities, measured to determine the amount of heat involved, really were the temperature differences required. This would be due to a non-

uniform distribution of heat. This matter has been investigated in connection with this work, and has been found to play an important part in the determination of the Peltier E.M.F. This question is discussed at some length in the next paragraph. Another probable advantage of this method is that the Joule heating-effect can be made much smaller than has been the case in some of the previous work. In this way the total range of temperature during a single determination is reduced.

Probable Sources of Error.—As will be observed by referring to the data given for the various couples, the compensating currents were frequently quite different. Several causes may be assigned for this, *e. g.*: (1) difference in rate of heat loss to surrounding bodies for the two calorimeters; (2) difference in the resistance of the immersed portions of the metals forming the junctions, due chiefly to the contact itself, and (3) difference in the heat *s*. This last is due principally to the stirrers either through heat produced by friction in the bearings or unequal stirring. Only the first of these can have any effect upon the final result [see discussion of equation (3)], unless *s* should vary during the course of the experiment. This may have happened occasionally, but would probably be as apt to influence the final result in one direction as in the other. Once or twice the speed of the stirrers changed owing to bad contact of the brushes with the armature of the motor. This would affect *s*. But another and more important effect due to such irregular action of the stirrers is that if the speed of the stirrers is varied in any way the steady temperature condition is upset, causing irregular movements of the galvanometer until a new temperature equilibrium is established. This difficulty actually arose and in consequence several runs gave unreliable results.

Inadequate stirring is a very probable source of error. In such cases the heat added to the liquid will not be distributed uniformly throughout the mass, but will remain in the neighborhood of the places where it is produced. In order to test this point a determination of the Peltier E.M.F. for the copper-bismuth couple was made without stirring the liquid. The result so obtained was 0.0084 volt, or a little more than half the true value. This, too, was the cause of considerable annoyance in the case of copper-platinum. Apparently the platinum foil which was used hung too close to the walls of the calorimeters, thus forming a sort of pocket where, owing to the resistance of the platinum, the liquid became hotter than the rest of the liquid in the vessel. Special precautions had to be observed in order to obviate this difficulty before any consistent set of measurements could be made.

To what extent the difference in rate of heat loss of the calorimeters may have affected the results it is difficult to say. One of the original calorimeters was discarded after it had apparently developed a fracture thus becoming a poor insulator. Afterward when some doubt arose as to the equality of this quantity for the two calorimeters which were used in all the later experiments, a test was made as follows: Both the calorimeters with contents were heated to a temperature of 65° C. and left standing uncovered in an atmosphere at 19° C. In 55 minutes the temperature of the calorimeter A had fallen to 30°.4 C., that of B to 29°.6 C. Several hours afterward both had come to the temperature of the surroundings. This shows that their rates of heat loss were practically equal, but these seem excessively large. The very rapid fall in temperature at first was probably due in part to the rapid evaporation of the kerosene at such temperatures. Another reason might be that a considerable proportion of the surface of the liquid was exposed to the air. Granting that even when the calorimeters are at approximately the temperature of the surroundings the quantity h is still rather large, it does not appear from equation (5) that any error in excess of the ordinary experimental errors should arise from disregarding the terms involving h.

SECOND, OR SHUNT-CURRENT, METHOD.

This method differs from the previous method in that compensation is accomplished by sending more current through one of the junctions than through the other, the difference in the Joule heating-effect being equal and opposite to that arising out of the Peltier effect.

Mathematical Discussion.—The mathematical computation of the Peltier E.M.F. in this case is quite similar to that for the preceding case. Using the same notation as before with the proviso that when I_a = current through junction A, and i_a = shunted current, then $I_a - i_a$ = current through junction B, we have

$$\frac{I_a^2R_a - I_aP - h_a\theta_a + s_a}{C_a} = \frac{(I_a - i_a)^2R_b + (I_a - i_a)P - h_b\theta_a + s_b}{C_b}.$$

Clearing of fractions and transposing we have

$$(1a)\quad \{(C_a + C_b)I_a - C_ai_a\}P = C_bI_a^2R_a - C_a(I_a - i_a)^2R_b - \theta_a(C_bh_a - C_ah_b) + (C_bs_a - C_as_b).$$

Similarly with current reversed

$$(2a)\quad \{(C_a + C_b)I_b - C_bi_b\}P = C_aI_b^2R_b - C_b(I_b - i_b)^2R_a - \theta_b(C_ah_b - C_bh_a) + (C_as_b - C_bs_a).$$

Adding, we obtain

$$(3a)\qquad \{(C_a + C_b)(I_a + I_b) - (C_a i_a + C_b i_b)\}P = C_b R_a\{I_a^2 - (I_b - i_b)^2\} + C_a R_b\{I_b^2 - (I_a - i_a)^2\} - (\theta_a - \theta_b)(C_b h_a - C_a h_b).$$

But, if $I_a = I_b$, this reduces to

$$P = \frac{C_b R_a(2I - i_b)i_b + C_a R_b(2I - i_a)i_a - (\theta_a - \theta_b)(C_b h_a - C_a h_b)}{C_a(2I - i_a) + C_b(2I - i_b)}.$$

Let us further assume that (1) $2I - i_a = 2I - i_b$, and (2) $C_a + c = C_b$. Then

$$P = \frac{C_a(R_a i_b + R_b i_a) + cR_b i_a}{2C_a + c} - \frac{(\theta_a - \theta_b)\{C_a(h_a - h_b) + ch_a\}}{(2C_a + c)(2I - i)}$$

$$= \frac{1}{2\left(1 + \frac{c}{2C_a}\right)}\left[R_a i_b + R_b i_a + \frac{c}{C_a}R_a i_b - \frac{(\theta_a - \theta_b)\left(h_a - h_b + \frac{c}{C_a}h_a\right)}{2I - i}\right].$$

By applying the binomial theorem and grouping terms as was done for the first method we obtain

$$(5a)\qquad P = \frac{1}{2}\left[R_a i_b + R_b i_a - \frac{(\theta_a - \theta_b)(h_a - h_b)}{2I - i} + \frac{c}{2C_a + c}\left\{R_a i_b - R_b i_a - \frac{(\theta_a - \theta_b)(h_a + h_b)}{2I - i}\right\}\right].$$

Notice the resemblance this equation bears to equation (5).

As a sufficiently close approximation for numerical work we may use the simplified equation

$$(4a)\qquad P = \frac{R_a i_b + R_b i_a}{2}.$$

The assumptions upon which this equation depends are: (1) $I_a = I_b$, (2) $2I - i_a = 2I - i_b$, and (3) disregard of the corrective terms. The first condition is easily realized. The third is the same as that used in deriving equation (4) and nothing further need be said regarding it. In order that the second condition may be assumed without appreciable error it is necessary that I shall be large in comparison with i. Since $P = Ri$, approximately, in order to fulfill this condition the resistance of the junction, R, must be considerable. This is also necessary for a quite different reason. If R were small it would be very difficult to ascertain its value, owing to the effect of the wires leading the current into and out of the bath.

Apparatus.—On this account, for the single determination of copper-nickel each junction consisted of two concentric spirals, one of copper and one of nickel wire. These were wound upon a light fiber frame which just fitted the bottom of the receptacle of the Dewar flask and extended up the sides for a distance of three centimeters. The actual junction was made near the bottom of the vessel. The resistance of each of these junctions was 0.4835 ohm, the wire used being No. 26 copper and No. 23 nickel. The nickel wires in the two junctions were connected by six strands of similar nickel wire twisted together. Heavy copper leads were soldered to the ends of the copper wires. These coils were completely immersed in the liquid. Otherwise the calorimetric arrangements,

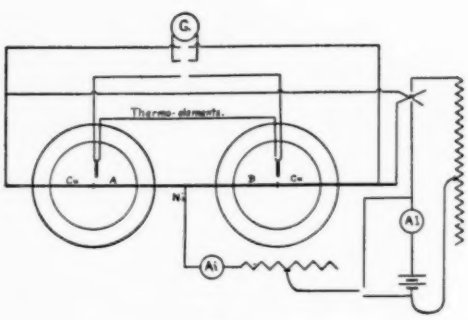

Fig. 6.

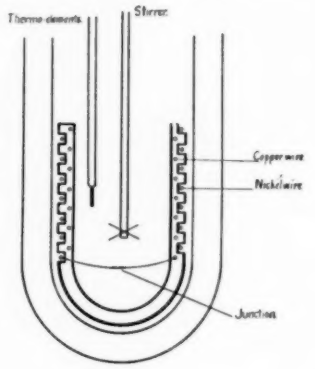

Fig. 7.

i. e., stirrers, thermo-elements, etc., were identical with those used for the previous method. For convenience in reading instead of using an ammeter to measure the shunt current it was measured by putting a milli-voltmeter across a standard resistance box through which the current was flowing. The resistance of the voltmeter was 340 ohms. By reading the voltmeter and knowing the box resistance the current could be computed. In most cases a potentiometer would probably be more suitable. By means of a three-way plug-key compensation could be effected in either calorimeter. The electrical connections are shown in Fig. 6, while Fig. 7 represents a cross-section of the bottom of a calorimeter with coil, thermo-elements and stirrer in place.

Probable Advantages.—An advantage which this method apparently possesses over the other is that the heat required to compensate the Peltier heat is produced in the wires which form the junction where the heat is being absorbed. Owing to the greater heat conductivity of the wires, neutralization of the Peltier effect should be accomplished much more readily than when it must all take place through the liquid. The

calorimetric conditions in the two calorimeters are as nearly as possible the same.

Probable Disadvantages.—The total temperature range during an experiment is greater for this method than for the preceding. This is obvious from the fact that the resistance of the junction is very much greater. This might give rise to a greater error since the heat loss is dependent, to a certain extent at least, upon the temperature range. The difficulties attendant upon the stirring are augmented. Otherwise the advantages and disadvantages of this method are substantially those of the preceding method.

Experimental Results.

Copper-Bismuth.

The copper-bismuth junctions were made of two strips of rolled copper plate 2.0×0.24 cm. cross-section, and a strip of bismuth cast for the purpose in the shape of an inverted U. The cross-section of the bismuth was 2.0×0.18 cm. This pair of junctions was the one used for all the preliminary tests of the method. Even the most crude measurements

Table II.

Copper-Bismuth.

I	i_a	i_b	$\frac{i_a^2 r_a}{4J}$	$\frac{i_b^2 r_b}{4J}$	P Expressed in Millivolts.
1.037	.1052	.1003	.00816	.00745	+15.61
1.038	.1081	.1015	860	762	16.22
1.957	.1459	.1388	831	756	15.87
.998	.1082	.1014	896	791	16.87
Mean—"hoop" coils					16.14
1.194	.0969	.0845	.00885	.00674	15.59
1.292	.1183	.0661	1219	382	16.01
1.243	.1172	.0664	1247	400	16.47
.502	.0695	.0505	1082	572	16.54
Mean—final coils					16.13

which were made did not differ by more than twenty per cent. from the value which was finally found for this couple. When the "hoop" coils were being used over two hours were sometimes required to determine with a fair degree of accuracy the amount of heat required to compensate the Peltier E.M.F. when the current was only sent in one direction. With the form of the coils finally adopted a complete determination could be made in one and a half or two hours. Four trustworthy determinations were made with the "hoop" coils ($r_a = 3.057$, $r_b = 3.072$),

and after these were replaced by coils of the final type ($r_a = 4.503$, $r_b = 4.509$) four other determinations were made. The data and results for these eight determinations are given below and separately averaged. All the values are for an approximate mean temperature of 18° C. Heat was absorbed when the current passed from bismuth to copper, and was given out when the direction of the current was from copper to bismuth. That is, using the same convention as Jahn and others, the sign of the Peltier E.M.F. is positive.

The Peltier E.M.F. between copper and bismuth is, therefore, +0.01613 volt at 18° C.

The extreme variation of these eight determinations is 8 per cent.; hence, the probable error is less than one per cent.

Copper-Silver.

The copper-silver couple was made of rolled copper strips, 1.0×0.25 cm. in cross-section, and a silver strip, 0.9×0.2 cm. in cross-section, rolled from a block of pure silver. Several trial runs were made, but because the magnitude of the Peltier effect was so small no satisfactory results were obtained. The values ranged from zero to + 0.00006 volt. These values are of the same order of magnitude as the experimental errors. The method finally adopted was to determine the rate of change of the deflection of the galvanometer while a compensating current of measurable magnitude was being supplied first to one heating-coil and then to the other. During this time no current was sent through the junctions. Then while no compensating current was being supplied, a current was sent through the junctions in one direction and the deflection at the end of every minute for an interval of from 20 to 30 minutes plotted. From this plot an average rate of change of deflection was obtained. The same was done with the current flowing in the opposite direction. Two such runs were made, the same current being sent through the junctions in each case.

When a current of 0.036 ampere was first sent through the heating-coil in calorimeter A and then changed to calorimeter B the change in the rate of change of deflection was 0.27 cm. per minute, the resistances of the coils being 4.503 and 4.509 ohms, respectively. From this it follows, as was pointed out in connection with the sensitiveness of the apparatus, that $\frac{0.036^2 \times 4.5 \times 60 \times 2}{0.27} = 2.59$ joules of heat added to one calorimeter will change the deflection of the galvanometer one centimeter.

The results for rate of change of deflection with the current flowing through the junctions were as follows:

TABLE III.

Copper-Silver.

	I	Direction of Current in A.	Rate of Change of Defl. per Min.
First run	4.65	Cu to Bi	+.02 cm.
Second run	4.65	Cu to Bi	+.028
First run	4.65	Bi to Cu	+.01
Second run	4.65	Bi to Cu	+.01

First run — diff. in rate of change of defl. per min. = .01 cm.

Second run — diff. in rate of change of defl. per min. = .018 cm.

Positive deflection indicates that the temperature of A is greater than that of B.

$$P \text{ (First run)} = + \frac{0.010}{0.27}\left(\frac{2 \times 0.036 \times 4.5}{4 \times 4.65}\right) = + 0.000023 \text{ volt.}$$

$$P \text{ (Second run)} = + \frac{0.018 \times 0.000023}{0.010} = + 0.000041 \text{ volt.}$$

The mean temperature of these two runs was approximately 18° C.

The Peltier E.M.F. between copper and silver is, therefore, +0.00003 volt at 18° C. The probable error is less than 0.00001 volt.

Notice that this result is very slightly positive, agreeing with that of Edlund, but is quite different from the value obtained by Jahn (see Table X. below).

A single determination at a temperature of 48° C. gave $P = 0$.

Copper-Aluminium.

The copper strips used were the same ones used in the case of copper-silver. Aluminium wire 0.5 cm. in diameter was used. The ends were flattened so that the immersed portions were 1 cm. wide, thus making their cross-section about the same as that of the silver. Only five runs were made. The first was merely a trial run and is omitted from the following table. The same heating-coils were used as in the previous experiment.

TABLE IV.

Copper-Aluminium.

I	i_a	i_b	$\frac{i_a^2 r_a}{4J} \times 10^9$	$\frac{i_b^2 r_b}{4J} \times 10^9$	P in Millivolts.	Approximate Mean Temp.
4.86	.0436	.0320	.4424	.2375	+.680	13.6° C.
5.12	.0463	.0337	.4713	.2501	.721	16.3
4.00	.0405	.0297	.4614	.2485	.710	18.1
5.60	.0461	.0347	.4271	.2423	.669	15.2
				Means	.695	15.8

The extreme range of these values is 7.4 per cent. of the mean. The probable error involved is about one per cent. We may, therefore, conclude that for copper-aluminium $P = +0.00070$ at 16° C.

Copper-Platinum.

The same copper strips were used as in the two preceding cases. The most suitable piece of platinum available was a piece of foil about 2 cm. wide and 33 cm. long. Its cross-section was approximately 0.0104 cm.^{2} Considerable difficulty was experienced in getting anything like consistent results with this couple. The difficulty no doubt arose from insufficient stirring of the liquid. Apparently the foil rested against the glass wall of the calorimeter in such a way as to separate a part of the liquid from the main body. This would be heated to a different temperature, and the amount of heat conducted to or from it by the remaining liquid would be dependent upon this difference in temperature. It was only after the greatest precautions had been taken to prevent the reoccurrence of this pocketing effect (such as folding in the corners of the foil and inserting small pieces of cork between it and the glass) that consistent results were obtained. Five determinations were made with the apparatus as finally adjusted. The fifth was a repetition of the second, which gave a result for P of + 0.00121 volt. These two determinations were made with a larger current than was used in the other three cases, and so the difficulty previously mentioned evidently reappeared in the second determination, which has been omitted on that account from the following table of results. In repeating this determination greater care was taken to insure good circulation of the liquid. Heating-coils of 1.49 and 1.505 ohms resistance were used so as to have larger compensating currents.

A current of 0.1097 ampere through the smaller resistance produced a change in the rate of deflection of the galvanometer of 0.494 cm. per minute. From this it follows that 2.18 joules of heat added to one calorimeter would change the deflection of the galvanometer one centimeter.

TABLE V.

Copper-Platinum.

I	i_a	i_b	$\frac{i_a^2 r_a}{4J} \times 10^3$	$\frac{i_b^2 r_b}{4J} \times 10^3$	P in Millivolts.	Approximate Mean Temp.
1.902	.0522	.0326	0.537	0.210	+0.747	17.0° C.
1.533	.0437	.0412	.464	.416	.880	16.3
1.035	.0445	.0195	.713	.138	.851	18.1
2.85	.0546	.0623	.390	.512	.902	17.2
				Means.....	.845	17.1

The extreme range of these values is 5.5 per cent. of the mean, hence, the probable error is about one per cent. For copper-platinum $P = + 0.00085$ volt at 17° C.

Copper-Nickel.

The apparatus used in this experiment has been described already in connection with the second method. The first two determinations given below were made on the day previous to the last two, and are considerably higher than the latter. The values corresponding to the higher temperatures are higher than the others, also one compensating current shows a marked tendency to increase with the temperature, the other to decrease. This indicates that the rate of heat loss to the surroundings was not the same for the two calorimeters. On the whole it seems that this method is not as satisfactory as the first method. This is doubtless due to the preponderance of the Joule heat.

TABLE VI.

Copper-Nickel.

I	i_a	i_b	P	Approximate Mean Temp.
0.650	.01463	.00950	+ .00583	19.2° C.
.701	1410	1520	708	25.0
.571	1206	1015	537	19.6
.611	1091	1329	585	24.0
		Means.....	603	22.0

The extreme variation of these values is 28.4 per cent. of the mean. Even assuming that the Peltier E.M.F. increases quite rapidly with the temperature the probable error must still be quite large. We shall take + 0.0060 volt to be the value of the Peltier E.M.F. between copper and nickel at 22° C.

SUMMARY OF RESULTS.

The values obtained for the Peltier E.M.F. for the couples investigated are tabulated below.

TABLE VII.

Metal Against Copper.	Peltier E.M.F. Expressed in Millivolts.	Temperature.
−		
Copper.....	———	———
Silver.....	0.03	18° C.
Aluminium.....	0.70	16
Platinum.....	0.85	17
Nickel.....	6.0	22
Bismuth.....	16.1	18
+		

JUNCTION DEFLECTIONS.

From the junction deflections it appeared that in the case of copper-bismuth the difference in temperature of the junctions at the end of a run varied from 0°.05 C. to 0°.1 C. For copper-silver and copper-aluminium the junctions appeared to have the temperature of the liquid. In the case of copper-platinum the results were variable, but certainly never greater than 0°.1 C. The maximum difference observed for copper-nickel was 0°.16 C.

THERMO E.M.F. AND THE PELTIER E.M.F.

In order to test the validity of Thomson's theorem, which has been mentioned already, viz., $P = T \frac{dE}{dT}$ where E is the thermo E.M.F. at the temperature T, the thermo E.M.F. of the various couples was determined. One junction was kept at a temperature of 0° C. by being

TABLE VIII.

Thermo E.M.F.

Metal Against Copper.	Resist.	Defl. in Cm.	Temp. Diff.	Thermo E.M.F. in Microvolts.	P Computed in Millivolts.
Bismuth	10,280	27.59	32.70	+55.07	
Bismuth	7,780	35.84	32.22	54.96	
Bismuth	7,280	37.43	31.75	54.49	
Mean (Abs. Temp. = 291)				54.84	+15.96
Silver	420	4.76	34.66	+ 0.366	
Silver	420	3.92	34.40	.306	
Silver	680	.58	32.08	.078	
Silver	480	.59	31.02	.058	
Mean (Abs. Temp. = 291)				.202	+ 0.06
Aluminium	680	21.80	29.52	+ 3.07	
Aluminium	420	39.15	31.58	3.11	
Mean (Abs. Temp. = 289)				3.09	+ 0.89
Platinum	3,280	4.72	39.50	+ 2.41	
Platinum	1,280	11.19	38.52	2.29	
Platinum	2,280	6.00	37.70	2.23	
Platinum	3,280	4.01	37.10	2.18	
Platinum	1,680	8.20	35.90	2.36	
Mean (Abs. Temp. = 290)				2.29	+ 0.66
Nickel	10,280	16.92	49.50	+21.61	
Nickel	12,280	13.82	48.54	21.50	
Nickel	8,280	19.92	47.22	21.48	
Nickel	10,280	15.31	45.14	21.44	
Mean (Abs. Temp. = 295)				21.51	+ 6.35

immersed in a bath of melting ice; the other junction was immersed in a water bath approximately as much above the temperature at which the Peltier E.M.F. was measured as 0° C. was below it. The E.M.F. was measured by connecting the thermo-element in series with a sensitive galvanometer and a standard resistance box. When used with the first three couples its deflection constant was 6.35×10^{-9} amperes per centimeter; with the last two the constant was 6.15×10^{-9}. Its resistance was 280 ohms. The galvanometer was badly damped when only a small resistance was in circuit with it and so the measurements with the copper-silver couple are not very reliable. The second pair of readings given for that couple were taken three hours after the first. The difference is probably due to a change in the temperature of some of the connections. In any event it is certain that the sign of the thermo E.M.F. of this couple was positive. Table VIII. gives the data obtained together with the computed values of the Peltier E.M.F.

Comparison of Results Obtained by Different Investigators.

In the following table the results of Le Roux, Jahn, Edlund (as computed in the first part of this paper), a few scattered results, and the results of the present investigation are grouped together. The calcu-

Table IX.

Results Obtained by Different Investigators, Expressed in Millivolts.

Metal Against Copper.	LeRoux.		Jahn.		Edlund.		Caswell.		Observed by Others.
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Antimony	− 5.64	.300							
Iron	2.93	.224	−3.68	−3.07	− 2.96	− 3.08			−3.06[1]
Cadmium	.53	.232	.72	.72	.16	.21			
Zinc	− .45	.614	.68	.41	− .01	− .02			
Copper	——	——	——	——	——	——	——	——	——
Silver			− .48	− .58	+ .03	+ .04	+ .03	+ .06	
Gold					.33	.50			
Lead					.50	.57			
Tin					.56	.82			
Aluminium					.70	.89	.70	.89	
Platinum			+ .37	+ .38	1.02	1.23	.85	.66	
Palladium					2.17	2.43			
Nickel			+5.07	+5.44			6.0	6.35	+6.75[2] +8.04[3]
Bismuth	+22.3	.263			+17.7	+17.6	+16.1	+16.0	

[1] Lecher's derived value of the Peltier E.M.F. between iron and *silver*.

[2] Barker.

[3] Cermak.

lated values have been obtained by means of Thomson's equation. The second column of values given for Le Roux contains the ratios of his values of the Peltier E.M.F. to thermo E.M.F. in relative units.

For all of these values I have aimed to retain only as many significant figures as seem to be justified by the accuracy of the experiments.

Physics Laboratory,
Stanford University,
April, 1911.

THE RECOVERY OF THE GILTAY SELENIUM CELL AND THE NATURE OF LIGHT-ACTION IN SELENIUM.

By F. C. Brown.

IN the July number of the Physical Review[1] it was shown that the general behavior of the four known varieties of selenium under the action of light could be explained by assuming that the different varieties were merely differently proportioned mixtures of three components which were in equilibrium according to the reaction

$$A \rightleftarrows B \rightleftarrows C.$$

In these considerations only the B component was a conductor of electricity. The amount of change of conductivity under the action of light at any instant was supposed to be proportional to the amounts of the changing components and to the rates of interchange according to the equations,

$$dB/dt = -(\alpha_2 + \beta_1)B + \alpha_1 A + \beta_2 C, \tag{1}$$

and

$$di/dt = k dB/dt, \tag{2}$$

and the value of the conductivity at any time after illumination was calculated to be

$$i = L/N + c_1 e^{m_1 t} + c_2 e^{m_2 t}, \tag{3}$$

where L, N, c_1, c_2, m_1, and m_2 represent constants for a light of a given intensity when the temperature and other functioning conditions are unchanging. These constants are determined solely by the rates of interchange as shown. The method of procedure was to assign values for the rates of interchange and then compute the value of the conductivity for different times of exposure. By the use of rates properly chosen such constants were obtained for equation (3) that its graph could be made to conform in a general way with all of the curve forms obtained experimentally with the four known varieties of selenium. It was stated that the action of light was merely the alteration of the rates of interchange, particularly an increase in the values of the direct rates of change α_1 and β_1, and further that the recovery from light-action was merely the process of restoration of the equilibrium amounts of the A, B and C kinds of selenium as the result of the smaller values of α_1 and β_1 prevailing in the dark.

[1] Phys. Rev., XXXIII., p. 1.

Therefore in the recovery of selenium equations (1), (2) and (3) must likewise be in agreement with the changes taking place, provided the proper values are assigned to the rates of interchange, and new limits are used in the integration such that

$$c_1 = \left[\frac{C_1}{\beta_1} + \left(\frac{L}{N} - B_1\right)\frac{1}{\beta_2 + m_2} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_2 - m_1}\right]$$

and

$$c_2 = \left[\frac{C_1}{\beta_1} + \left(\frac{L}{N} - B_1\right)\frac{1}{\beta_2 + m_1} - \frac{L}{N\beta_2}\right]\left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_1 - m_2}\right],$$

where B_1 and C_1 are the respective amounts of the B and C kinds at the instant the recovery begins. In the action of light the corresponding constants B_0 and C_0 represented the amounts of the same components when the selenium was in equilibrium in the dark.

Inasmuch as only the B component is conducting we may simplify our discussion by supposing that the units of conductivity are of such magnitude that B may be used interchangeably for either the amount of the component or the conductivity.

Whereas it was shown in the previous paper that the general behavior of all the known varieties of light-positive and light-negative selenium could be explained by the proposed theory, it will be shown in this paper for one of the light-positive varieties, viz., that found in the Giltay selenium cell, that the change of conductivity during both exposure and recovery can be explained quite accurately by the same theory. The Giltay cell furnishes evidence more convincing than some varieties of selenium in that some of its rates of interchange are very close to the critical values. A slight alteration of the rates by certain temperature changes will transform the experimental recovery curve from one type to a second distinct type of curve. And it will be shown that these two types of recovery curves are precisely what might be predicted from theory. The Giltay cell is particularly adapted for a critical test of the theory also because of its stability, sensibility and uniformity. If kept in the dark most of the time and subjected to no unusual treatment the selenium cells of the high resistance type made by Giltay maintain approximately their initial resistance and initial light-sensitiveness. It is thought that any work with the Giltay cell can be repeated with greater certainty than can work with any other light sensitive selenium on the market. As many can testify a special skill is required to produce selenium with specific rates of change. Mr. Giltay states that after making selenium cells for thirty years he still has surprises in his results. My high sensibility selenium cells are more sensitive than the Giltay

cells but they possess neither stability nor uniformity. The selenium cell used in these analytical investigations is the same one mentioned in the preceding paper.

Exposure and Recovery Curves.

Selenium is difficult to investigate in that so many agencies alter its conductivity, and it is not always easy to eliminate all except the one under investigation. For example in studying light-action, there is a certain heating effect and also a change in the pressure on the selenium. The change in pressure may be due to change in volume of the selenium between the semi-fixed electrodes, as a result of the light-action and the temperature-action. The magnitude of these two effects is not easy to ascertain. In our theory we must consider these effects as due directly to light-action. Probably the effects just mentioned are not larger than the observational errors. In addition the radioactivity of the atmosphere, the moisture, and the barometric pressure alter the equilibrium condition and consequently the conductivity. In order to minimize the disturbing influences the selenium cell was placed in a kerosene oil, or paraffin oil, bath which was kept in motion continuously during observations by a stirring device. See Fig. 1. The kerosene oil bath was surrounded by a water bath which was also kept in motion by a stirring device, run by a motor. The temperature of the bath was regulated by an electric heating coil. The source of illumination was a 24 watt tantalum lamp with frosted globe. The lamp was inverted in a beaker which stood in the water bath. Unless otherwise mentioned the distance of the lamp was kept fixed at about 10 cm.

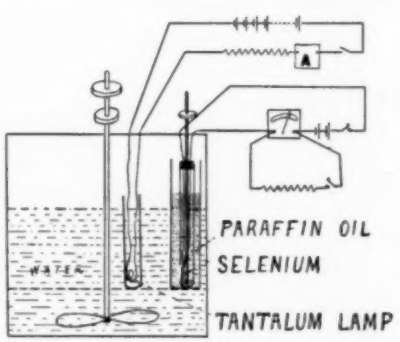

Fig. 1.

The intensity of the light was regulated by varying the resistance in series with the lamp. The large bath was kept light tight. It was considered that the advantages of this apparatus were that the selenium would remain at about constant temperature during observations and that all the surroundings except the lighted lamp would be at the same temperature as the selenium. There were fewer difficulties due to stray light than I have observed hitherto with other apparatus. The conductivity was read directly from a Siemens and Halske needle galvanometer in series with the selenium cell and a two volt storage battery.

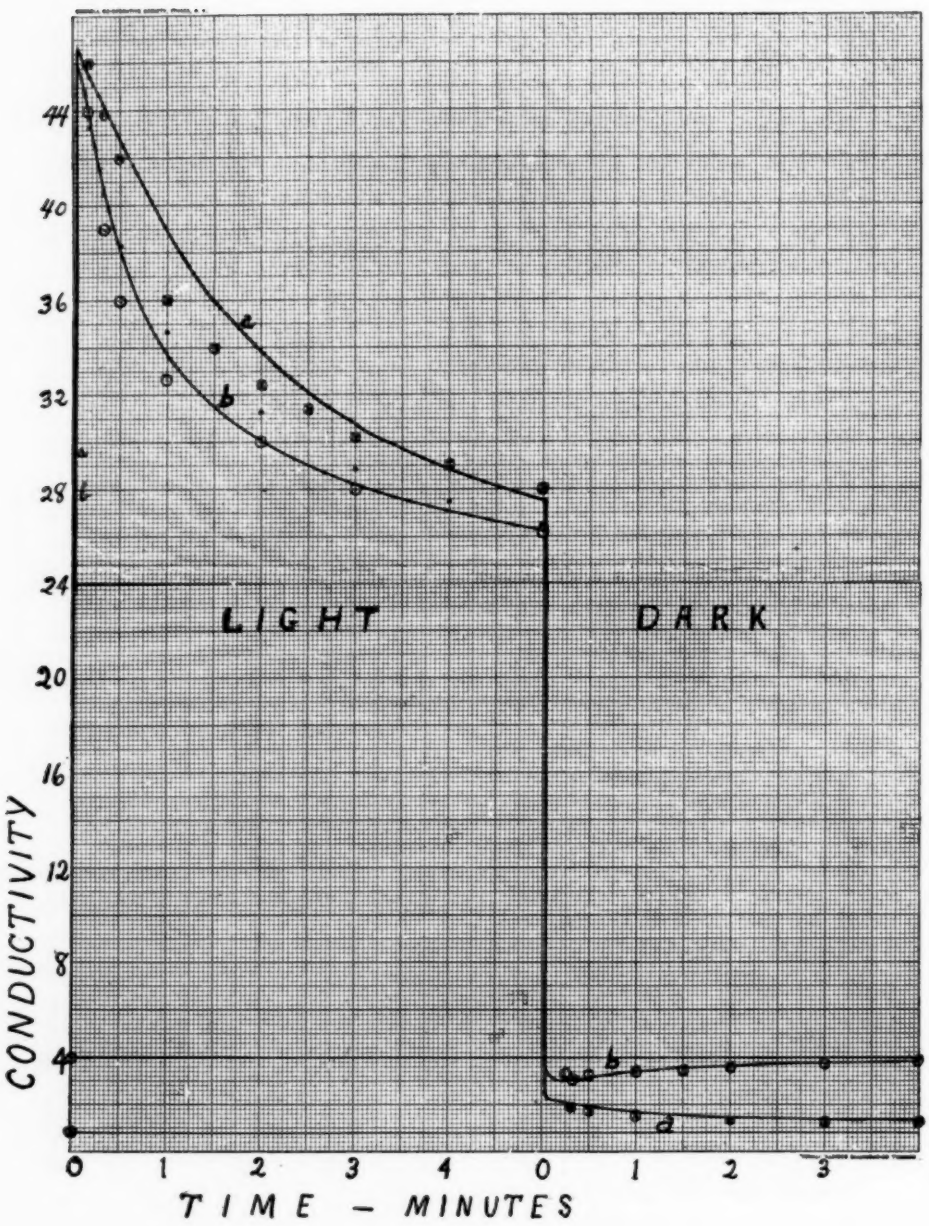

Fig. 2.

a represents the theoretical values of the conductivity during exposure and recovery at 18° C.; *b* is the theoretical curve for 52° C.; ⊗ represents the observed values of the conductivity at 18° C.; ⊙ represents the observed values at 52° C.; ● represents observed values at 28° C.

Observations were taken with the selenium at 18° C., 28° C., and 52° C., when the intensity of the illumination was that given by the tantalum lamp when the heating current was 0.43 ampere. The observations are shown in Fig. 2. It was impossible with the apparatus described to observe the more rapid changes which took place within a fraction of a second. The rapid changes due to the same illumination were measured by another method to be mentioned later in the paper. It may be noted that the conductivity under intense illumination is almost independent of the temperature. At the higher temperature the decrease of conductivity occurs somewhat more rapidly thus bringing the conductivity below that at lower temperatures. This may seem rather strange when it is noted that the conductivity at 52° C. begins at 4.0, which is five times that at 18° C., and two times that at 28° C. These facts are in substantial agreement with the results published in the previous paper, under less favorable circumstances. The maximum change of conductivity at the lowest temperature is about 110 times that in the dark, while the equilibrium conductivity is only 63 times that in the dark.

The recovery for the three temperatures is remarkably different. At 18° C. the first observation that could be made accurately was after 20 seconds, when the conductivity was more than twice that required for equilibrium in the dark. Although readings could not be taken accurately before 20 seconds, yet it was certain that at the end of the fifth second that the conductivity was not more than three times the dark value. After the first few seconds the remainder of the conductivity was regained very slowly. After four minutes it was fifty per cent. too high and after ten minutes the conductivity was yet 40 per cent. above the final value. In the recovery at 28° C. there was no observed difference in the rapid change but the slow change became much faster. After 15 seconds the conductivity was only 47 per cent. above the final value and after four minutes it was only eight per cent. The results that show that the rapid change taking place during recovery is not altered much by temperature will be given later.

At 52° C. the first observation that could be made showed that the conductivity was less that the final value as shown by curve *b*, Fig. 2. In fact it was about 25 per cent. too low for equilibrium. By further observations as shown in the same figure, the conductivity increased slowly during recovery until the equilibrium value was reached. After four minutes the value was 7 per cent. below equilibrium and after 8 minutes it was 5 per cent. Roughly the conductivity seems to increase during recovery only slightly faster than it decreased at the lower tempertures. But how much the difference is depends upon the temperature.

At some temperature between 28° C. and 52° C. the selenium is in what might be called a critical condition, so far as the slow changes are concerned in the recovery. The slightest alteration in pressure, temperature, or other influencing agents might change the character of the recovery curve. In fact the selenium may be said to be in a critical condition at either 28° C. or 52° C. for a ten second exposure at 52° C. will give a recovery curve of like character to the one shown in Fig. 2 for 28° C.

These two types of recovery in the Giltay cell which are conditioned

TABLE I.

Giving the rates of change necessary to explain the observed values of the conductivity during exposure and recovery at different temperatures.

	18° C.	
	During Illumination.	**During Recovery.**
α_1	.054	0.00134
α_2	12.0	12.0
β_1	0.9	.018
β_2	0.004	.004
A	5,550 } Equilibrium values	11,200 } Values for com-
B	25 } in the light.	.8 } plete recovery.
C	5,625 }	3.6 }
Equation of conductivity	$B = 25 - 46.2e^{-12.5t} + 22e^{-.0075t}$	$B = 0.8 + 24e^{-12t} + 1.25e^{-.004t}$

	52° C.	
	During Illumination.	**During Recovery.**
α_1	0.3	0.025
α_2	12.0	12.0
β_1	0.3	.07
β_2	0.009	.009
A	1,040 } Equilibrium values	1,892 } Equilibrium values
B	26 } in light.	4 } in the dark.
C	860 }	30 }
Equation of conductivity	$B = 26 - 42e^{-126t} + 20e^{-.016t}$	$B = 4 + 23.1e^{-12t} - 1.1e^{-.01t}$

by temperature are very striking and they offer a rather severe test to our theory. However these diverse types can be explained theoretically by assuming that the action of the temperature change is merely an alteration of the rates of interchange. This was predicted in the previous paper referred to. In Table I. are given the rates of change during exposure and also during recovery which will explain the curves as obtained from observations when the selenium was at 18° C. and also at 52° C. The constants and the equations of conductivity result from

the rates of change, when calculated by the aid of the set of equations given in the previous paper and in this paper. Other rates might satisfy the experimental curves as well as the ones chosen. I can only state that the ones recorded are the best I could find. Everything depends on the rates. The quantity of only one kind of selenium must be taken arbitrarily to suit the units of conductivity chosen. The quantities of the other kinds both in the dark and in the light are calculated. As stipulated the sum of the three kinds can not change. In practice the value of the B kind for equilibrium in the dark was chosen to agree with the observed conductivity of the selenium in the dark. Then rates of change were found which would give the maximum and the final conductivity observed in the light. After obtaining agreement between theory and experiment for exposure it was fortunately very easy to obtain the same agreement for recovery. Afterthought showed that this is what should be expected. In fact if perfect agreement were obtained for exposure, then we should know almost without trial what rates should be proper to explain the recovery observations. The recovery and exposure, as a study of the theory will show, are closely correlated. The graphs of the equations in Table I. are represented in Fig. 2 by the continuous curves. It will be observed that the conductivity curve is always continuous.

It is surprising indeed that the agreement between theory and experiment is so close as shown in Fig. 2. This particular case was chosen as the most difficult one to explain that could be obtained with any variety of selenium under any conditions. The extreme range of the conductivity and the peculiarity of the curves would have made a much worse agreement satisfactory. It is not certain that the rates given in Table I. are more than approximately correct. However later thought shows that they are of the right order of magnitude and probably vary only in the second place from the true values. But what is most important at this stage of our investigation is to find out what light and temperature do to the rates of change, and to inquire if the things that happen are consistent and reasonable. It may merely be noted here from Table I. that light increases the direct changes α_1 and β_1 and that a temperature rise increases all the changes except possibly the reverse rate of change α_2. The relative action of light and temperature as shown is of much interest but we shall reserve discussion on this point until later in the paper when we have considered more comprehensive data.

CHANGE OF CONDUCTIVITY DURING EXPOSURE AND RECOVERY FOR FAINT ILLUMINATION.

In the discussion just preceding the intensity of the light may be considered as relatively great although it was probably not larger than 32 cp. at 10 cm. In general it is important to check theory and experiment under conditions that allow the greatest change, but in this instance it is also quite necessary to find agreement where the illumination is not intense and where there is consequently only a small change in the conductivity.

In order to predict what difference may be expected between faint illumination and intense illumination, we must first define what we mean by faint and intense. We will consider the wave front of light as speckled at any instant with light and dark spots of small dimensions, and that the light spots travel about over any uniformly illuminated surface in such a manner that after a few seconds any one finite area shall have been hit by the same number of light spots as any other equal area on the surface. This is the well known spotted wave front theory[1] proposed by Sir J. J. Thomson,[2] and others. The intensity will be defined as the average number of light spots per unit area at any instant. Thus the essential difference between the action of an intense light and a faint light on selenium lies in the difference in the number of particles acted on at any instant, or we may say in the difference of rate of action. If light acts on selenium until saturation is produced there will be just as many particles struck and changed by light per second as recover per second. Light of small intensity acts on only a small number of particles per second, while an intense light acts on a relatively large number. Every particle that is struck with faint light will change just as much as it would if struck by an intense light, but before it is struck a second time it will be almost recovered. The interval between successive impingements of a faint light on the same small region is relatively large. And so on the average for all the particles, they will be almost recovered all the time. The result is that the rates of recovery for faint illumination will be smaller than for intense illumination. More will be said on this point in the discussion of the experimental results obtained.

The observations with faint illumination were taken under about the same circumstances as those previously described with intense illumination. The source of light was the same tantalum lamp when it was carrying 0.11 ampere as heating current. As before the entire surface

[1] See paper by Sir J. J. Thomson.

[2] Proc. Camb. Phil. Soc., XIV, p. 41, 1908.

of the selenium was illuminated. The intensity was so regulated that the conductivity would be about doubled by the light. The temperature was about 26° C. The observed conductivity at all times during both exposure and recovery is shown in Fig. 3. In Table II. are given the

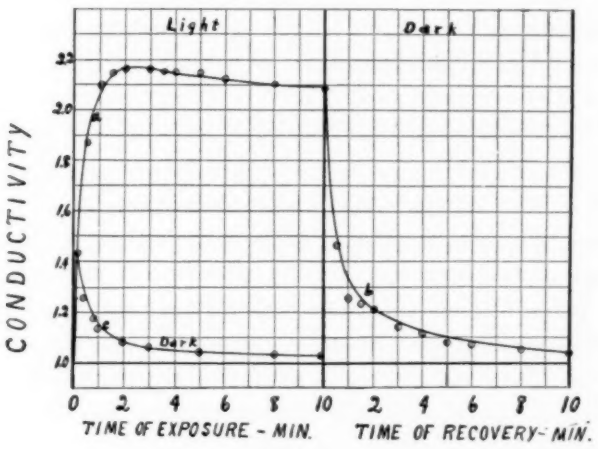

Fig. 3.

Exposure and recovery curves with faint illumination. *a* is the theoretical curve for exposure; *b* and *c* are theoretical curves for recovery; ⊙ represents the observed values.

rates of change during exposure and recovery which would cause the conductivity to vary along the continuous lines *a*, *b*, and *c*. The agreement is found to be within the limits of experimental error and is as good as could be hoped for. It is particularly noteworthy that the same rates of change explain the recovery at the end of a ten-second exposure that explain the recovery at the end of a ten-minute exposure.

TABLE II.

Giving the constants and resulting equations necessary to explain the exposure and recovery curves when the selenium is exposed to faint illumination at 26° C.

During Illumination.				During Recovery.	
α_1	0.004			0.00132	
α_2	0.02			0.02	
β_1	0.01			0.0053	
β_2	0.003			0.003	
A	15.6	Before	10.2	13.9	Values at end
B	1.0	illumi-	2.86	1.42	of ten sec.
C	1.8	nation.	5.4	3.11	exposure.

Values at end of ten min. exposure.

$B = 2.06 - 1.17e^{-.033t} + 0.17e^{-.003t}$. $B = 1 + 0.83e^{-.03t} + 0.23e^{-.0026t}$ for 10 min. exposure.

$B = 1 + 0.35e^{-.03t} + 0.08e^{-.0026t}$ for 10 seconds exposure.

The initial values of the three kinds of selenium for recovery after a ten-second exposure are calculated by the aid of the equations given in

the previous paper. It must be remembered that the initial conditions during recovery are determined by the rates during illumination and conversely that the initial conditions during exposure are dependent on the rates during recovery, as well as the time of recovery. No experiments were made to check theory and experiment where the selenium had only partially recovered but I have no doubt whatever but that the agreement would be as satisfactory as the other results.

THE RECOVERY WITH DIFFERENT DURATIONS OF EXPOSURE.

We have shown for intense light at certain temperatures and for a given period of illumination that the reverse change between the A and B components is large compared with the reverse change between B and C. This suggests at once that the recovery of B into A may be determined directly by measuring the resistance changes over such short intervals of time that no appreciable amount of the C kind is changed into B. In order to predict what change in B may be expected, we will substitute the rate values during recovery and also the amounts of the components, as found in Table I. into equation (1). This gives

$$dB/dt = -(12 + .14) \times 25 + 0.0025 \times 1923 + 0.004 \times 100.$$

We observe from this that so long as B is large compared with unity, that the change in B should be almost proportional to the amount of B present at any instant, regardless of the amount of A and C. This conclusion may obviously be stated in the following form: the change of conductivity for short intervals during recovery divided by the conductivity should be a constant for large values of B and constant illumination.

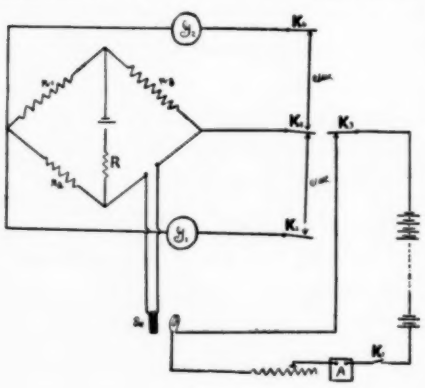

Fig. 4.

To test the above relation the selenium was exposed to the tantalum lamp, carrying 0.35 ampere, for various lengths of time, and the mean conductivities were measured during the last 0.1 second of exposure and during the first 0.1 second of recovery. This was accomplished by a modification of the method of measuring fluctuating resistances described by Brown and Clark.[1] Two galvanometers instead of one were used, as shown in Fig. 4. The pendulum that operated the galvanometer

[1] PHYS. REV., XXXIII., p. 53, 1911.

keys also opened the lighting circuit. The first galvanometer was thrown into circuit only during the last 0.1 second of exposure and the second galvanometer was likewise in circuit only during the first 0.1 second of recovery, after the selenium was darkened. By the usual calibration the deflections were translated into the equivalent mean conductivity during the interval in question. The period of one of the galvanometers was increased by adding a lead rider to the moving coil. This enabled one observer to read both galvanometers. The selenium cell was left in the bath arrangement previously described. The temperature was 22° C. An hour or more elapsed between observations to allow the selenium to recover. The results of the observations are shown on the curves in Fig. 5. The points on the upper curve resulted from observations made on the first galvanometer, and the points on the lower curve were calculated from the deflections of the second galvanometer. The difference between any pair of observations recorded on the two curves divided by the higher value gives the mean fractional part of the conductivity recovered between zero and 0.1 second. This fractional part or per centage recovery is recorded in Fig. 5 for each pair of observations. I was surprised myself at the constancy of these percentages. The conductivity varies by at least forty per cent. and yet it is doubtful if the percentage recovered varies as much as one per cent. when the time of exposure varies from 0.4 second to 240 seconds. As the first value is low however there may be some doubt as to the constant percentage recovery for exposures of only a fraction of a second.

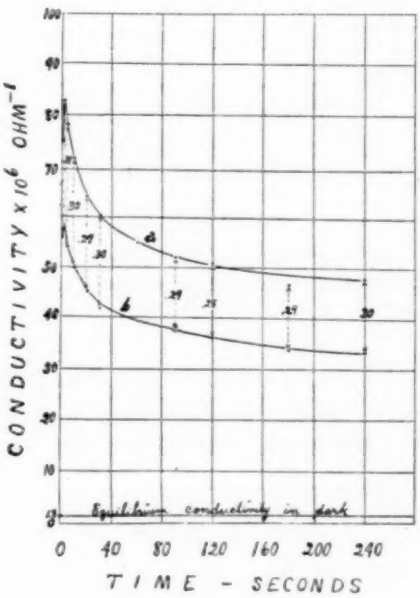

Fig. 5.

The upper curve (*a*) shows the conductivity for any period of illumination from 0.4 second to 240 seconds. The lower curve (*b*) shows the conductivity of the selenium after recovering 0.05 second following any period of illumination. Conductivity in dark 1.3.

The mean percentage recovery recorded during the first 0.1 second was about 30. If we assume that this value was reached in 0.05 second, then we obtain for the rate of change of B into A, $\alpha_2 = 12$. This is in agreement with the curves in Fig. 2, for which no observations were

taken directly for periods less than ten seconds. In fact the result here recorded was used as an aid to obtain the correct rates of change to explain the observations in Fig. 2. By the same method recorded in this section the recovery during 0.1 second was measured at 40° C., and it was found that the fractional part recovered was 34 per cent. This indicates quite directly what was shown in Table I., that the value of the reverse rate of change α_2 is altered little if any by temperature changes.

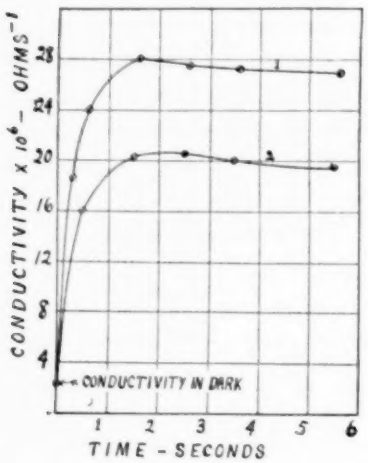

Fig. 6.

(1) Conductivity before recovery. (2) Conductivity after recovering during 0.1 sec.

In Fig. 6 is shown the percentage recovery for exposures between zero and six seconds. In taking these recorded observations the selenium was not placed in a bath, but nevertheless they are substantially in agreement with the other results. The intensity of the light was less than in the other instance, and the pendulum keys were so arranged as to give the recovery after 0.1 second and not the mean recovery between 0 and 0.1 second.

THE VARIATION OF THE RATE OF RECOVERY WITH THE INTENSITY OF EXPOSURE.

A comparison of the data in Tables I. and II. indicates that the rapid rate of change α_2 varies greatly with the intensity of illumination. After the thorough investigation mentioned in the last sections was made, which showed that the value of α_2 did not vary with the time of exposure within very wide limits, it was thought advisable to investigate the effect of varying intensity by the same method. The same apparatus referred to in Fig. 4 was used. However, when the change of resistance was small the first galvanometer was used to measure the equilibrium resistance in the dark and the resistance at the end of a three minute exposure by the ordinary Wheatstone's bridge method. The second galvanometer measured by its throw the mean change of resistance during the first 0.1 second after the light was extinguished. The period of illumination was kept constant and the intensity was varied by changing the heating current in the lamp. As I have not yet considered quantitatively the effect of varying the intensity of the light, I have not yet taken the trouble

to interpret the intensity in the usual units. A sufficiently accurate notion of the intensity for our present discussion may be estimated from the value of the heating current and also from the change of resistance of the selenium. The results of the investigation are given in Table III.

TABLE III.

Time.	Current in Lamp Amperes.	Temperature.	Potential Across Cell, Volts.	Time of Exposure.	Resistance in Dark.	$1/B$ Resistance in Light.	Deflection.	$\Delta B \times 10^9$ Ohms^{-1}.	$\frac{\Delta B}{B}$ Mean Percentage.
10:55 A. M.	0.15	27.8°C.	2	3 min.	680,000	159,000	6.1		
11:45					680,000	158,000	4.0		
1:00 P. M.					700,000	156,000	4.0		
						Mean	3.7	0.016	2.5
9:02 A. M.	0.20	28.0	2	3	740,000	74,000	14.5	0.11	
9:53					710,000	74,000	14.6	0.11	
									8.2
1:15 P. M.	0.45	27.5	2	3	700,000	16,300	74.		
3:50					677,000	16,900	73.		
								2.79	46.5
6:30	0.33	27.7	2	3	703,000	28,200	64.	1.05	29.6
7:25	0.355		2	3	710,000	23,000	73.	1.44	33.1
9:40	0.40	27.9	2	3	680,000	19,700	76.8	2.04	40.2
10:55	0.3	27.5	2	3	705,000	34,000	67.0	0.72	24.0
12:04	0.25	27.8	2	3	683,000	49,400	39.3	0.31	15.3
2:38	0.22	28.1	2	3	660,000	62,000	28.0		
5.30							24.0		
								0.18	11.2

The value of $\Delta B/B$ varies from 2.5 per cent. for the faintest light measured to 46.5 per cent. for the most intense light. It may be stated without qualification that $\Delta B/B$ increases with increased intensity. The rate of change as calculated from the value 0.025 is only slightly larger than the value given for α_2 in Table II., where the conductivity was somewhat less. This is as it should be.

In obtaining the data in Table III. the character of the light varied as well as the intensity did, and the same may be said for the comparative observations in Figs. 2 and 3. Just what difference arises from the altered character of the light can not be predicted with any certainty, but the assumption that the characteristic difference in the results noted is due to a variation in the light intensity can not be far wrong. It was shown in the previous paper[1] in a general way that when the character of the light source was practically constant, and when the intensity of illumination was varied by varying the distance of the source that the

[1] PHYS. REV., XXXIII., p. 1.

time required for the maximum conductivity to be reached during exposure increased with decreasing intensity.

The Effect of Short Exposures.

The effect of short exposures to either intense or faint illumination is to produce the changes that take place rapidly but it does not follow that the recovery should be correspondingly less for short exposures, than it would be for long exposures. If there is a large increase in the conductivity as a result of a short exposure, during exposure the conductivity component changes both into the A kind and the C kind, and it will be noted from Table I. that the rate of transformation into C is relatively quite large. It follows that before equilibrium is reached all of the C kind must be retransformed back into the B and C kinds, which is of course a slow process. Again this notion is confirmed by the equations of the conductivity, in which the exponential coefficients are determined solely by the rates of change, while the constants c_1 and c_2 are determined both by the rates of change and the time factor.

That the preceding explanation for the recovery from short exposures is probably the correct one, may be inferred further from the observations shown in the curves in Fig. 7. The selenium at 20° C. was exposed to a very intense light, roughly a 32 cp. tungsten lamp at 7 cm. distance for a period of 0.35 second. This period was just about sufficient to allow the selenium to reach its maximum conductivity, *i. e.*, the condition when there was the maximum amount of B present. This was one hundred times the amount of B present in the dark equilibrium condition. After 0.85 second only about 85 per cent. of the conductivity change is seen to be recovered. And even after 60 seconds it was still twice what it should be for equilibrium in the dark at that temperature. Probably the most surprising fact is that both theory and observation show that it requires longer for selenium to recover its conductivity after exposure to a faint light than it requires to recover from a long exposure to a very intense light.

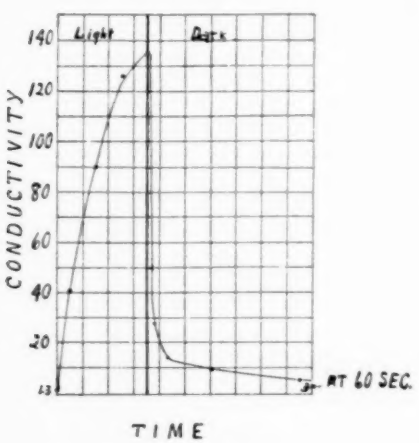

Fig. 7.

Each division represents 0.1 second.

For high temperatures also the recovery from very short exposures is similar to that shown in the last figure, but more rapid. But for longer exposures the recovery is like that shown in Fig. 2. This is in general agreement with the theory. For short exposures there is only a small amount of the *B* kind transformed into the *C* kind and consequently the conductivity should be continually diminishing. If the exposure is continued then there is such a large amount of the *C* kind produced that the *B* kind first diminishes rapidly below the dark value in order to approach equilibrium between *A* and *B*, and then increases slowly until the equilibrium value is reached. Here caution is urged against assuming that selenium is in equilibrium merely because the equilibrium value of the conductivity is reached. In case the selenium is in apparent equilibrium, but in reality not, the sensitiveness to light is diminished just as might be expected if the amount of the *A* kind present were too small. For a long time this diminished sensitiveness to light was very puzzling to me.

THE RECOVERY FROM THE EFFECTS OF HIGH POTENTIAL DIFFERENCES.

It was stated in two earlier papers[1] that the change of conductivity of selenium by high potential differences was of the same nature as the change by light This conclusion was based largely upon the fact that the light sensitiveness of the selenium diminished as the potential difference between the electrodes was increased, and also upon the fact that

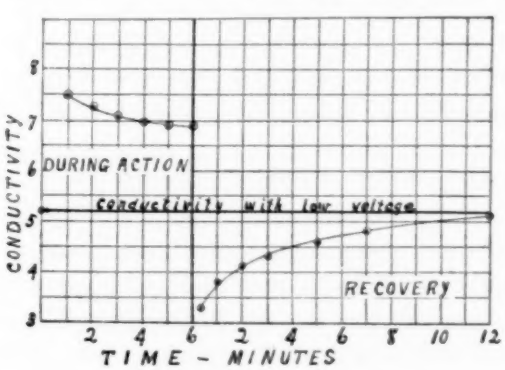

Fig. 8.

Curves showing the conductivity of the selenium during the action of 152 volts potential difference and during the recovery.

both agencies acted in such a manner as to first increase the conductivity and then to decrease it. Further consideration shows that both effects

[1] PHYS. REV., XXVI., p. 273, 1908, and XXXIII., p. 1, 1911.

are similar, in that they alter the rates of interchange and consequently increase the amounts of the B and C kinds. But the rates are altered in quite different proportions by the two effects. Light acts chiefly on the rates between the A and B components while the high potential acts about as much on the B and C components as on the others. Observations that were taken during action and recovery with 150 volts are shown in Fig. 8. I have not yet succeeded in obtaining any accurate notion of the rapidity of the more rapid change. Before an accurate comparison of the rates can be made it will be necessary to measure the rapid changes.

THE INTERPRETATION OF THE RESULTS.

We have shown that the proposed kinetic reaction theory agrees in a general way with all the varieties of selenium known and further that when tested in particular with one of the most complicated the agreement is all that could be hoped for. It has not been necessary to impose any conditions that are unreasonable or that complicate the simplicity of the argument. But having established the theory thus far to a fair degree of accuracy, it is of interest to inquire what may be its further physical significance.

It has not been necessary to assume that more than one of the three components are conducting and further it has not been necessary to assume that light acts in the least degree on the reverse rates of change. In both these respects the theory is less complex than when it was first proposed. These facts have been tested for intense light at two widely varying temperatures. In fact the temperature difference was so great that the initial conductivity in the dark differed by a factor of five. The light was so intense that the conductivity in one instance had a maximum value 110 times that in the dark. That only the direct changes are necessarily altered by light was also shown for light so faint that the maximum conductivity was only twice what it was in the dark. There can be little doubt but that for light effects one hundred times smaller than this, we would also find that only the direct rates would necessarily be altered. The generality of this conclusion is not only interesting but also a big advance in our theory. It should simplify the physical interpretation and at the same time reduce the difficulties in the mathematics.

TABLE IV.

Ratio of Rates in Light to Dark.	Intense Light at 18° C.	Intense Light at 52° C.	Faint Light at 22° C.
α_1'/α_1	40	12	3
β_1'/β_1	50	4.3	1.9
α_2'/α_2	1	1	1
β_2'/β_2	1	1	1

That light may act on the rates in about the same way for intense light as for faint light is shown in Table IV., which is compiled from the data in Tables I. and II. To distinguish between rates, those prevailing during light action are primed.

Attention should be called to the fact that at different temperatures and with different intensities of light, we do not suppose the existence of the same total amount for the three components. The meaning of this is not certain. The total amount might possibly vary with temperature but this could hardly be the case with varying intensity. Possibly the amounts considered are partially fictitious, and that as previously alluded to, an intense light acts on a large proportion of the components present, while a faint light acts on only a relatively small proportion at any instant. It may be suggested here that the different initial rates of change that analysis shows to exist in the four known varieties of selenium, may in some cases arise from a difference in the attractive power of the components for certain molecular aggregates either in the solid or gaseous state. Obviously the impurities might modify the rates unequally for the different components. I hope to develop this idea further later in explaining certain unstable samples of selenium.

In the original paper it was assumed that the light was of uniform intensity throughout the selenium at any instant. Now in order that our analysis shall apply to the facts, we must understand that the light shall have what might be called only an average uniformity.

The rates of change that are given in this paper assume that light acts throughout the conducting layer of selenium. The fact that the rates are so consistent with each other and that they so satisfactorily explain the observations would lead one to suspect that the above assumption is not far wrong.

The Effect of other Agencies.

A study of the tables shows that our previous predictions concerning the similarity of the action of light and temperature still seem to be consistent. So far as light action is concerned it is necessary to assume that temperature alters the direct rates α_1 and β_1 to a very large degree. However in addition to this, temperature produces a slight change in the reverse rate β_2 and possibly also a minor change in conductivity of which no account is taken in our theory. The fact that temperature alters three of the rates will probably make it easy to explain the numerous temperature coefficients that are possessed by the different varieties of selenium. Temperature no doubt acts throughout the conducting layer of selenium. This being assumed we have at once an easy method of estimating the relative depth of penetration of selenium by light.

The behavior of selenium under the action of pressure, radium, X-rays and other agencies should aid us in the interpretation of our results. The fact that selenium recovers very slowly from radium action as pointed out by Brown and Stebbins or X-ray action as pointed out by Miss MacDowell[1] can be explained satisfactorily if we assume that these agencies have compared to intense light a low frequency for any point region. It seems that this is the most reasonable assumption to make. Further if selenium is suddenly relieved from a very high pressure it should recover much more rapidly for the rapid part of the change, than it does from illumination of ordinary intensity. What observations we have made on this point indicates this high rapidity of recovery for either small or large pressures. However, we were not prepared in 1907 to measure this rapid rate. Further investigations on the rate of action by other agencies will no doubt show that the proper assignment of rates of interchange will explain the larger part of the changes taking place, but the values that are obtained may modify our intrepretation materially.

SUMMARY OF CONCLUSIONS.

1. Without making any allowance for the fact that the light does not probably penetrate throughout the conducting layer of selenium, the theory agrees fairly satisfactorily with the observations over a wide range of temperature and light conditions.

2. Only one of the three components is conducting.

3. Very direct experiments show that for at least one case the change in the conductivity is proportional to the amount of the changing component.

4. Temperature action in the Giltay selenium cell is essentially the same as light action but not identical to it.

5. More careful and more extensive work should be carried out to determine the full significance of all the rates of interchange.

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[1] PHYS. REV., XXX., p. 474; also paper by M. Perreaux, Comptes Rendus, Vol. 129, p. 956.

THERMAL CONDUCTIVITY AT HIGH TEMPERATURES.

By M. F. Angell.

Introduction.

With the growth of the electron theory and its application to the flow of heat in metals the measurement of thermal conductivity becomes of greater interest. The determinations, up to the present time, have been confined within narrow limits of temperature and the object of this investigation was to determine the thermal conductivity of a few metals over a wide range. The first measurements at high temperatures were made by Forbes,[1] using the well-known "Forbes bar method," on wrought iron at temperatures of 0°, 100°, 200° and 275° C.; giving a decrease in thermal conductivity from .207 at 0° C. to .124 at 275° C. Tait[2] and Mitchell[3] used the same method, but found an increase in conductivity with temperature, which is undoubtedly in error, as shown by the later work of Jäger and Diesselhorst.[4] Lorenz[5] heated a rod at one end by contact with a large slab and determined the temperature gradient by means of thermocouples inserted in holes along the rod; the source of heat was then removed and the temperature gradient determined when the rod was cooling. Between 0° C. and 100° C. he found an increase in conductivity with temperature for aluminum, brass, copper and german silver; a decrease for antimony, bismuth, cadmium, iron, lead and zinc; and a constant for magnesium. Baillie,[6] with the Forbes method, determined the thermal conductivity of nickel between 0° C. and 100° C. to be .132 and found this value to be changed only in the third decimal place at a temperature of 200° C. Jäger and Diesselhorst[4] used a method suggested by Kohlrausch,[7] which consisted in heating a rod with a constant electric current; the ends of the rods being in contact with large baths, a steady flow of heat was maintained from the center to the ends. The temperature was measured at three points along the rod by means of thermocouples inserted in holes. Determinations were made

[1] J. D. Forbes, Athenäum, p. 1012, 1852.
[2] P. G. Tait, Trans. Roy. Soc. Edinb., p. 717, 1880; Phil. Mag. (5), 12, p. 147, 1881.
[3] A. C. Mitchell, Trans. Roy. Soc. Edinb., p. 435, 1887.
[4] W. Jäger u. H. Diesselhorst, Abh. d. Phys.-Techn. Reichsanstalt, 3, 269, 1900.
[5] L. Lorenz, Wied. Ann., 13, p. 422, 1881.
[6] T. C. Baillie, Trans. Roy. Soc. Edinb., 39, p. 361, 1897–98.
[7] F. Kohlrausch, Ztschr. f. Instruementk., 18, 139, 1898; Drude's Ann., 1, 145, 1900.

on a large number of materials at 18° C. and 100° C.; an increase in thermal conductivity with temperature was shown by aluminum, constantin, gold, manganin, palladium, platinum and tombac; and a decrease by bismuth, cadmium, iron, copper, lead, nickel, silver, steel and zinc.

A NEW METHOD FOR THE DETERMINATION OF THERMAL CONDUCTIVITY.

In this investigation a new method, suggested by Professor C. E. Mendenhall, was used for the determination of thermal conductivity of metals at high temperatures. If a long cylindrical rod is heated electrically the temperature over a short distance l, symmetrically situated with respect to the ends, is approximately uniform and this approximation may be made as close as we please by increasing the length of the rod. In this central section, l, Fig. 1, the energy flow is then radial,

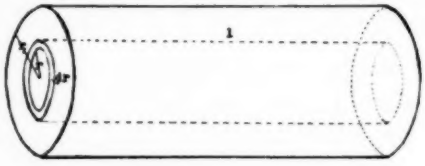


Fig. 1.

i. e., from the center to the circumference, and the quantity passing through any concentric cylindrical surface, of radius r and length l, is given by $-2\pi rl\lambda dT/dr$; where λ is the thermal conductivity and dT/dr the temperature gradient at r. When a steady state is reached we have

$$\pi r^2 lEI = -2\pi rl\lambda dT/dr;$$

integrating

$$\frac{EI}{2}\int_0^{r_1} r dr = -\lambda \int_{T_2}^{T_1} dT,$$

or

$$\lambda = \frac{EIr_1^2}{4(T_2 - T_1)}, \qquad (1)$$

where r_1 is the radius of the rod, E the fall of potential along one centimeter, I the current density, which is assumed constant over the cross-section and T_2 and T_1 are the temperatures at the center and circumference of the rod respectively. If the measurement of the fall of potential along l is difficult, as with alternating current, a separate determination of resistance at different temperatures may be made and IR substituted for E in the equation, R being the specific resistance.

The above discussion is on the assumption that the variation of specific resistance, due to the variation of temperature from inside to outside of the rod, may be neglected. As a closer approximation we may assume the radial variation of resistance to be proportional to r^2, as would follow to a first approximation from equation (1); substituting E/R for I we may write

$$R = R_2 - \alpha r^2,$$

where R_2 is the resistance at the center of the rod. Then

$$\int_0^r \frac{E^2}{R_2 - \alpha r^2} 2\pi r l dr = -2\pi r l \lambda dT/dr .$$

and

$$\frac{E^2}{2\alpha} \log \frac{R_2 - \alpha r^2}{R_2} = r\lambda dT/dr .$$

Dividing the equation by $E^2 r/2\alpha$ and integrating we obtain

$$\int_0^{r_1} \log \left(1 - \frac{\alpha}{R_2} r^2\right) \frac{dr}{r} = \int_{T_1}^{T_2} \frac{2\alpha}{E^2} \lambda dT$$

or

$$\lambda = \frac{E^2 r_1^2}{R_2 4(T_2 - T_1)} \left[1 - \frac{\alpha r_1^2}{4R_2} + \frac{\alpha^2 r_1^4}{9R_2^2} \cdots\right]. \qquad (2)$$

In this case the term outside the bracket is the value of λ obtained above. By substituting the values of α and R_2 as approximately known for any metal, the terms containing these quantities are seen to be negligible for rods less than 2 cm. in diameter.

For a hollow cylinder, where r_2 and r_1 are the inside and outside radii respectively, we have

$$\pi(r^2 - r_2^2) l E I = -2\pi r l \lambda dT/dr.$$

Integrating

$$-\lambda \int_{T_2}^{T_1} dT = \frac{EI}{2} \int_{r_2}^{r_1} (r^2 - r_2^2) \frac{dr}{r}$$

and

$$\lambda = \frac{EI}{2(T_2 - T_1)} \left[\frac{r_1^2 - r_2^2}{2} - r_2^2 \log \frac{r_1}{r_2}\right]. \qquad (3)$$

This is the formula used in the present investigation. As the energy is measured in watts, λ must be multiplied by .239 to reduce it to cal./cm. sec. degree.

When alternating current is used, these formulæ will not apply to magnetic substances as the "skin effect" must be considered in expressing the distribution of current inside the rod. The problem of determining

thermal conductivity under these conditions was found too complicated for the present investigation and determinations on these substances were limited to temperatures such that the magnetic properties, as indicated by the presence of an appreciable skin effect, had disappeared.

Experimental Details.

The determination of thermal conductivity requires the measurement of three quantities: the dimensions of the rod, energy flow and temperature difference between the inside and outside of the rod.

1. *Dimensions of the Rod.*—Preliminary experiments showed that on heating a hollow rod six inches long the temperature was quite uniform over a length of one centimeter at the center. In order to decrease the heat flow to the ends of the rod the central hole was made larger at the ends and to within 1½ centimeters of the center; this increased the heat generated each side of the center by increasing the resistance and made the temperature uniform over a greater length. Determinations of temperature inside the rod at about 1000° C. showed a variation of approximately two per cent. over a length of two centimeters and less than one tenth of one per cent. over one centimeter. The measurement of temperature gradient did not require a uniform temperature over so great a length, but in the resistance determinations a uniform temperature was assumed over a length of one centimeter. The inside hole, .168 cm. in diameter, was drilled from each end and carefully reamed. In order to correct for any eccentricity, which might be present, temperature measurements were made at the ends of several radii in the central section. The outside diameter was approximately 1.2 cm., but varied slightly in the different determinations, due to polishing the surface. In order to eliminate oxidation the rod was enclosed symmetrically in a large, water-cooled cylinder from which the air could be exhausted.

2. *Energy Flow Measurements.*—As sufficient direct current was not available a welding transformer was used, capable of furnishing 1700 amperes at 2½ volts. The current was measured by means of a Weston ammeter accurate within one per cent. and a current transformer designed by Professor E. Bennett, of the engineering department of the university, accurate within one per cent. The measurement of low voltages with alternating current being unreliable a separate determination of the resistance at different temperatures was made, using direct current, and the resistance-temperature curve was plotted. For the resistance measurements the same rods were used as for thermal conductivity, with the outer diameter greatly reduced. The temperature for the resistance measurements was determined by a thermocouple in-

side the rod midway between the ends. The ammeter and voltmeter were calibrated in terms of laboratory standards. In order to eliminate the peltier effect at the point of contact of the potential terminals with the hot rod the terminals were made of fine wires of the same material as the rod; these being held parallel to each other and against the rod by brass frames. The distance between the terminals, approximately one centimeter, was measured by means of a micrometer gauge.

3. *Temperature Measurements.*—The temperatures were determined by two thermocouples, of No. 40 platinum and platinum-rhodium wire, standardized by using the boiling point of sulphur, the freezing point of antimony and the melting points of silver and gold. The electromotive forces of the thermocouples were measured on a potentiometer made for this work, the slide wire being one meter in length with six additional resistances each equal to that of the wire. One millimeter indicated 2 microvolts or about .2 degree and estimates were made to one tenth of this quantity. For small temperature differences the galvanometer deflections were also calibrated and could be estimated to one fifth of a microvolt or approximately .02 degree centigrade.

Measurement of Temperature Inside the Rod.—For the measurement of temperature inside the rod, the fine wires leading to the thermocouple were enclosed in small quartz tubes running longitudinally through the inside of the rod, with the junction itself midway between the ends. Breaking the quartz tube at the center appeared to make no difference in the temperature determinations.

Measurement of the Temperature of the Surface.—The greatest difficulty was to insure that the outer couple indicated the actual temperature of the surface; for this reason fine wires were used and, drawn diagonally

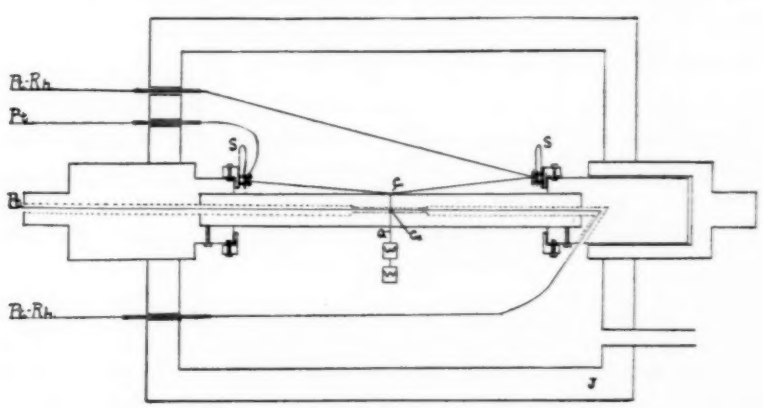


Fig. 2.

SS, springs; *CC*, thermocouples; *WW*, weights; *Q*, quartz fiber; *J*, water-jacket. Springs were rotated from position shown

across the rod by two springs, were held close to the surface along its entire length (Fig. 2). The thermal junction was rolled in steel rolls to a thickness of .01 mm. and forced into contact with the highly polished surface by the small springs and by small weights hung over the rod by means of quartz fibers. A uniformly radiating surface in the neighborhood of the couple was found to be most important, so that either the rod must be platinum plated or the thermal junction covered with a layer of the same material as the rod. On account of the difficulty of platinum plating the second method was adopted; a piece of the same material as the rod was rolled in the form of a ribbon to a thickness of .01 mm. A short piece of this was then placed over the couple and held in contact with the rod by the quartz fibers and small weights, producing a uniform surface over the entire rod. Under these conditions the difference in temperature between the inside and outside of the rod

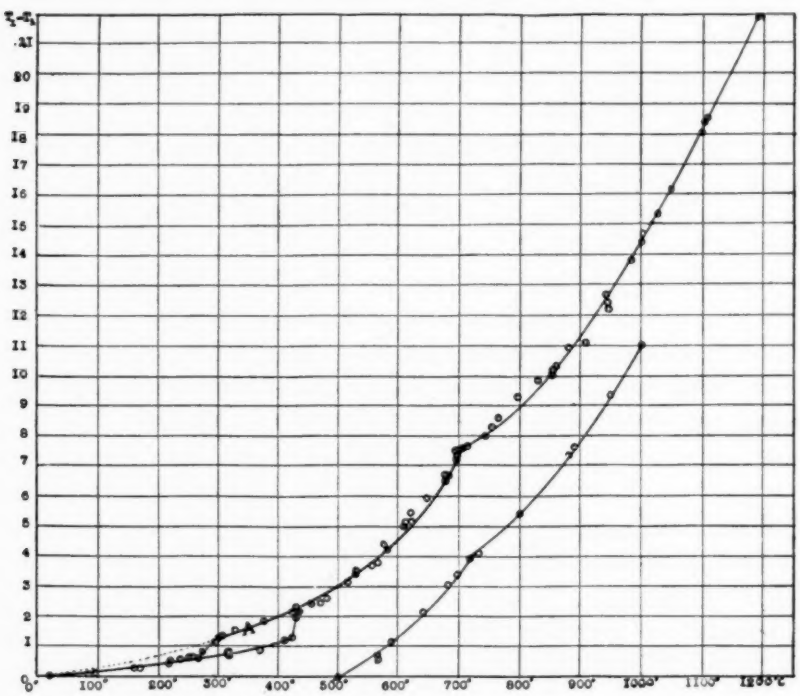


Fig. 3.

Variation of temperature-difference with temperature.

was determined differentially at different temperatures and the curve plotted (Fig. 3, *A*); this curve could be repeated after rotating the outer couple around the rod, shifting slightly the inner couple or replacing the original couples by new ones from the same wire. The formation of a

thin layer of oxide produced but small effect. The curve *B*, Fig. 3, of no value in the determination of thermal conductivity, was obtained when the nickel foil covering the couple was removed and the couple exposed. The platinum, being a poorer radiator than the nickel, acted as a shield at this point and the temperature was raised; below 500° C. the outer couple indicated a higher temperature than the inner. Poor contact between the outer ribbon and the rod was quickly indicated by the unsteady readings of the couple. In the work with nickel the dissociation temperature of nickel oxide was reached, due to the low pressure, at about 900° and the protecting ribbon was so completely welded to the rod that the two could not be distinguished. With the couple welded to the rod and imbedded under the surface to a depth of .01 mm. the quartz fibers were removed and the thermal conductivity curve determined with the rod rotated 120 degrees and 240 degrees from its original position. The agreement of curves indicated a symmetrical radiation from the surface of the rod in all directions. The rod was also heated when exposed to the air and a thick layer of oxide formed; under these conditions the temperature gradient was increased as the radiation from the surface was greater than before and temperature differences, for given inside temperatures, were greater than indicated by the curve (Fig. 3, *A*). There was, however, a corresponding increase in the energy required to maintain this temperature and the computed thermal conductivity curve coincided with that found when a bright surface was used. As criteria for deciding that the true value of thermal conductivity is obtained by this method we have, with a bright surface, the repetition of the temperature difference curve, on rotating the rod, rotating the thermocouple around the rod, displacing slightly the inner couple or on replacing the original couples by new ones from the same wire and the repetition of the thermal conductivity curve with a different radiating surface and therefore a different temperature gradient. Considering all the errors in measuring the dimensions of the rod, temperature, resistance and current, even when alternating current is used the error should be less than two per cent. above 300° C., while with direct current the error should not be over one per cent.

Results. Nickel.

Two rods of nickel from the same piece were used. This was obtained from H. Boker, New York, as the best available and no analysis has yet been made; probably however, it contains from two to three per cent of cobalt. The first rod was not heated above 700° C., and, within experimental error, gave the same temperature difference between the inside and outside, at a given inside temperature, for different positions

of the couple around the rod and with the first couples replaced by new ones of the same wire. The second rod was of the same dimensions as the first and the curve showing temperature difference between the inside and outside of the rod for different temperatures coincided with that for the first rod and is shown in Fig. 3, *A*. The sharp rise in the curve at about 300° C. indicates the temperature at which nickel loses its magnetic properties; a change in the slope of the curve is also seen at about 700° C. From the electrical resistance at different temperatures, as shown in Fig. 4, the thermal conductivity at different temperatures

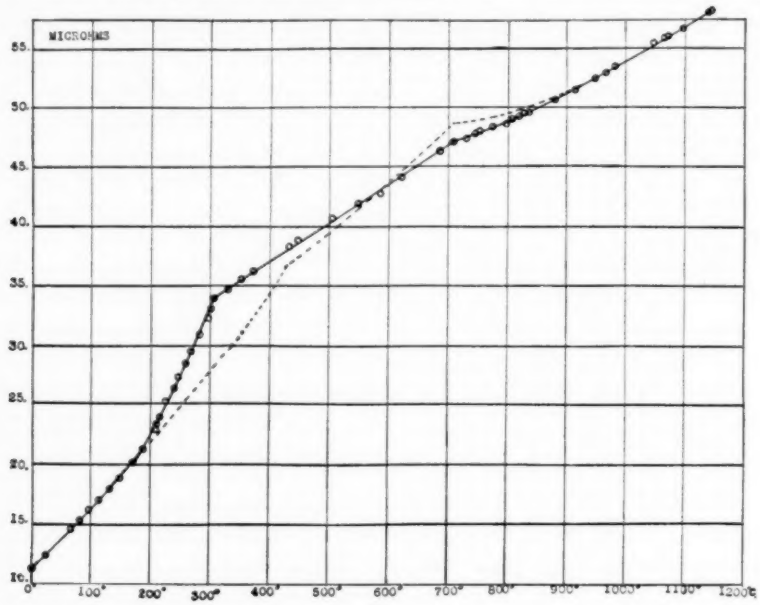


Fig. 4.

Resistance of nickel between 0° and 1200° C. The dotted line shows the resistance after sudden cooling; the full line, the resistance on first heating.

was computed and the curve drawn (Fig. 5). If this curve is prolonged to zero it will pass very nearly through the values of thermal conductivity given by Jäger and Diesselhorst, viz., .1420 at 18° C. and .1374 at 100° C. A prolongation of the curve may also be obtained by extending the temperature difference curve, shown by the dotted line in Fig. 3, *A*, as if undisturbed by skin effect and computing the thermal conductivity, at any temperature, from the current required to produce this temperature and the temperature difference determined from the curve. The second method is less reliable, however, as it does not allow for the fact that a greater amount of energy is required to produce a given inside temperature than if there were no skin effect. If the values of thermal conductivity found by Jäger and Diesselhorst at 18° C. and 100° C. are

assumed for this specimen there is no change in the slope of the thermal conductivity curve at the temperature where nickel loses its magnetic properties, where, however, the change in the electrical conductivity is very marked. The thermal conductivity decreases more rapidly as the temperature increases up to 700° C., where its value is .069. At this point there is a most decided change in slope and the thermal conductivity decreases very slowly to 1225° C., with a value of .058 at this temperature. From the abrupt change in the slope of the curve one would conclude that an allotropic form of nickel is formed at about 700° C.

The temperature difference curve (Fig. 3, *A*) was repeated many times, and it was found that the readings did not check with the original curve between 300° C. and 420° C. after the rod had been suddenly cooled from high temperatures; the form of the new curve is shown by *C*, Fig. 3. Due to the sudden cooling the magnetic transformation point, as indicated by the sudden rise in the temperature difference curve, was changed from 310° C. to about 420° C. After annealing at about 900° C. and cooling very clowly to room temperature the transformation point was found at about 290° C., lower than at first. With this treatment it was possible to shift the transformation point at will between these limiting temperatures, 290° C. and 420° C.

As there is a decided change of slope in the electrical resistance curve at the magnetic transformation point the change in this curve was investigated when the transformation point was shifted; it had already been noticed that a smooth resistance curve could be passed through the points determined on the first heating of the rod, while those determined on cooling were not on this curve. The form of the curve as first determined and after sudden cooling is shown in Fig. 4, the transformation point being at 310° C. in the first case and approximately 420° C. in the second. With the transformation point between these limits the temperature-resistance curves were determined and when the transformation point was between 350° C. and 400° C., as assumed by Harrison[1] and Marvin,[2] the resistance between 0° C. and 350° C. could be approximately represented by a parabola. For a lower transformation point the form of the curve was shown by Knott[3] and is nearly a straight line up to 200° C. where the slope increases and continues nearly constant to the transformation point. Investigations of the magnetic properties of nickel by different observers have shown the transformation point to vary between 270° C. and 400° C.;[4] the lower values were commonly

[1] E. P. Harrison, Phil. Mag., June, 1904.

[2] C. F. Marvin, PHYS. REV., 30, p. 522, 1910.

[3] C. G. Knott, Trans. Roy. Soc. Edinb., p. 33, 1888.

[4] Honda and Shimizu, Phil. Mag., Oct., 1903.

supposed to be due to impurities, but from this work appear to depend more upon the treatment of the specimen. The probable explanation of the fact that different observers have not obtained more nearly the same magnetic transformation point is the lack of annealing at a sufficiently high temperature.

It is customary to associate a change in the properties of a substance with a change in molecular structure and metallurgists have found an alpha, beta, gamma and even a delta state for iron and an alpha and beta state for nickel, but I believe this is the first indication of a third allotropic form, "gamma," for nickel, which appears at about 700° C. The change in the thermal conductivity curve at this temperature is very decided, as is shown in Fig. 5; the change in the resistance curve

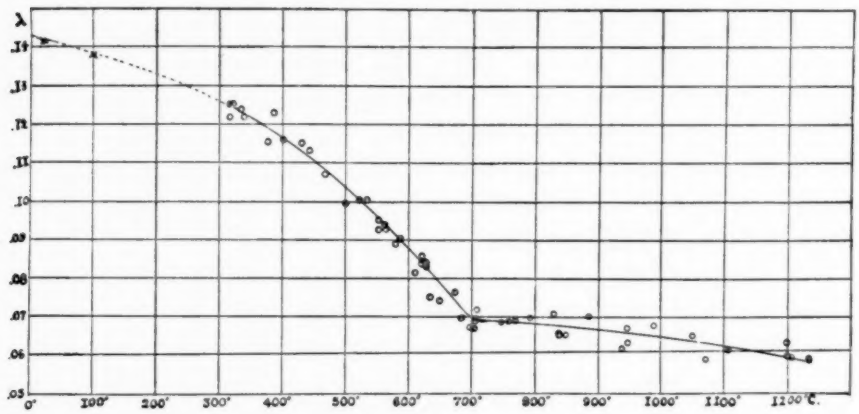


Fig. 5.

Thermal conductivity of nickel, 300°–1200° C. ××, values of Jäger and Diesselhorst.

is not marked when the transformation point is in the neighborhood of 300° C., but with the transformation point at 420° C. a decided change of slope is observed. In the resistance curve given by Sommerville,[1] this change of slope is not apparent, but in a later paper[2] where the slope of the curve is given the change is plainly shown. Apparently there is a molecular rearrangement at about 700° C., producing an allotropic form of nickel, which is carried down by quenching and causes a change in the resistance and magnetic properties.

In order to compare the elasticity under different conditions a test was made with a Shore scleroscope, by measuring the rebound of a small hammer dropped upon the specimen; using the same rod as for the electrical and thermal conductivity experiments, the rebound was found to be much less after quenching, in the ratio of 7.2 to 14.

[1] A. A. Sommerville, Phys. Rev., 30, p. 532, 1910.

[2] A. A. Sommerville, Phys. Rev., 31, p. 261, 1910.

Aluminum.

A single aluminum rod, of the best commerical grade, 99 per cent. pure, was tested. The determination of thermal conductivity, shown in Fig. 6,

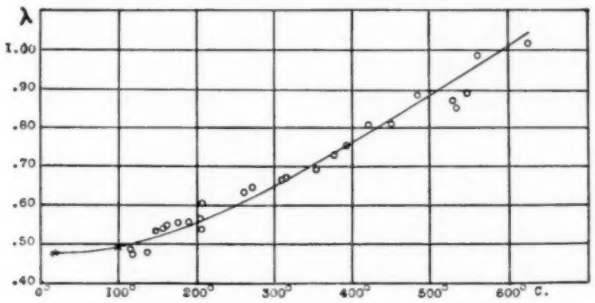


Fig. 6.

Thermal conductivity of aluminum. ××, values of Jäger and Diesselhorst.

was less satisfactory than with nickel, on account of the low electrical resistance and high thermal conductivity, which increases with temperature; both of these properties tending to decrease the temperature difference between the inside and outside of the rod. The determinations near 100° C. agree well, however, with the value .492, which was found

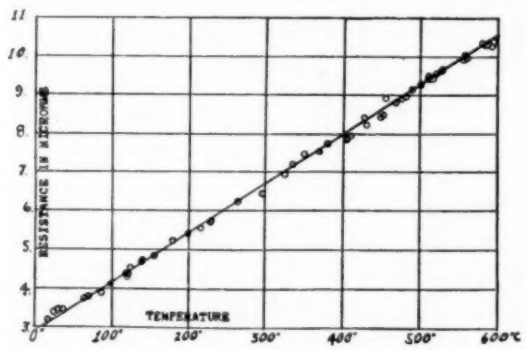


Fig. 7.

Resistance of aluminum.

by Jäger and Diesselhorst at this temperature and their values were used to prolong the curve to zero. Their values may be assumed for this specimen as the purity of the aluminum was about the same in both cases. The thermal conductivity of aluminum increases more rapidly at high temperatures than between 18° C. and 100° C., increasing from .49 at 100° C. to 1.0 at about 600° C.

In order to insure good contact with aluminum, where the protecting strip could not be welded to the rod, a small weight with a very sharp

point was dropped repeatedly upon this outer strip and very fine holes made into the rod, then with a small hammer the strip was pounded down tight and smooth over the surface. By this method very many small portions of the outer strip were forced into the holes in the rod and the strip held in close contact.

The electrical resistance curve (Fig. 7) coincides very closely with that given by Sommerville[1] for a good grade of commercial aluminum.

Summary.

1. A new method of determining thermal conductivity has been tried and shown practicable with metals at high temperatures.

2. The thermal conductivity of nickel, between 300° C. and 1200° C. and of aluminum between 100° C. and 600° C. has been determined.

3. There is no constant ratio between electrical and thermal conductivities for these metals at high temperatures. At high temperatures the thermal conductivity of aluminum increases, and of nickel up to 700° C. decreases, more rapidly than from 0° C. to 100° C.; above 700° C. the thermal conductivity of nickel decreases very slowly up to 1225° C.

4. A third allotropic state for nickel has been found at about 700° C., with a change in the form of the electrical and thermal conductivity curves at this point.

5. The magnetic critical temperature of nickel has been shown to be shifted through a range of one hundred and thirty degrees by heat treatment; annealing from high temperatures giving a low value and sudden cooling producing values as high as 420° C.

6. The electrical resistance of nickel between 0° C. and 1200° C. and of aluminum between 0° C. and 600° C. has been found and, for nickel, the change in the form of the curve which accompanies a change in the magnetic critical temperature due to heat treatment has been determined. It was found that the temperature-resistance curve could be approximated by a parabola only when the critical temperature was in the neighborhood of 370° C.

7. The elasticity of nickel was greatly reduced by quenching, but could be increased to its original value by annealing at high temperatures.

In conclusion I wish to express my most sincere thanks to Professor Snow for placing the necessary apparatus at my disposal and to Professors Mendenhall and Mason for their kindly interest and helpful suggestions throughout this investigation.

Physical Laboratory,
University of Wisconsin,
July, 1911.

[1] A. A. Sommerville, Phys. Rev., 31, p. 261, 1910.

ON THE FATIGUE OF METALS SUBJECTED TO ROENTGEN RADIATION, IN THE PRESENCE OF CHEMICALLY ACTIVE GASES.

By Edward G. Rieman.

THE recent experiments by Professor More[1] and Dr. Gowdy,[2] show that metals, subjected to Roentgen radiation, suffer changes of secondary radiation, in a manner somewhat similar to that found by Hallwachs[3] in the case of metals acted upon by ultraviolet light. This action has been designated by the term fatigue.

For example, it was found that a freshly polished iron disk, when exposed to X-rays, in an atmosphere of air, gave after three hours exposure, a secondary radiation which was four per cent. greater than the original. On the other hand, a disk of lead exposed for the same length of time, under the same conditions, showed a decrease in secondary radiation of three per cent.

Furthermore, it was found that chemical change of the surface was necessary in order to have fatigue take place. Metals exposed in the inactive gas, carbon dioxide, showed no fatigue. Disks whose surfaces were old and chemically stable gave no fatigue when experimented upon in an atmosphere of air.

As the above authors have worked only with air and ozone, both of which form oxides on the surfaces of metals, it is desirable to study the effects which occur in atmospheres of other chemically active gases and vapors.

Practically the same apparatus and methods were employed in the following experiments as were used by Dr. Gowdy. A brief description of these can be given as follows:

The X-ray tube, T, which can be rotated about a vertical axis is contained in a large lead-covered box. Two thick brass tubes, P_1 and P_2, direct the rays into two similar cubical ionization chambers. An aluminum gauze, G, is supported by ebonite insulators and is held firm at a distance of one centimeter from the disk holder, H. This holder is designed to carry the disk and is held in place by the sulphur plug, S. Highly insulated and metallically shielded wires connect the holders

[1] More, Phil. Mag., XIII., p. 708.

[2] Gowdy, Phys. Rev., Jan., 1910, p. 62.

[3] Hallwachs, Sitzungsbericht der Ges. der Wissensch. zu Leipzig, LVIII., 1906, p. 341.

to the Wilson electroscope, E. The two gauzes are maintained at opposite potentials of 80 volts, this being sufficient to produce saturation. The process of taking readings was as follows.

Two disks of the same metal, one called the standard and the other, the trial plate, were placed in the holders. By rotating the X-ray tube, the radiation falling upon the disks was adjusted so as to make the two currents set up in the ionization chambers exactly equal; this balance could be recognized when no deflection of the electroscope occurred. When the balance had been obtained, electrical connection between the electroscope and the holder of the trial plate was broken by means of the switch, W, and a time deflection reading, called, t_1, was taken in order to get a quantity proportional to the amount of secondary radiation given off by the standard plate. Owing to the existing electrical balance, this amount was also necessarily equal to the amount given off by the trial plate. Several readings for both plates showed this to be the case.

The standard plate was then shielded while the other remained exposed to the X-rays. At intervals of an hour, trials were made to see whether or not the balance still existed; if it persisted, both plates were evidently still giving off equal amounts of secondary radiation However, if the balance were destroyed, a time deflection reading, t_d, was taken, and this reading served to indicate the increase or decrease of secondary radiation given off by the trial plate. A substitution of the readings, t_1 and t_d, in the formula developed by Dr. Gowdy gave the percentage fatigue suffered by the exposed plate.

For further details reference may be made to the papers cited.

Although this balance method is in itself accurate, certain refinements in the method of taking readings have been adopted for the following experiments. It is evident, that a true reading for fatigue can only be taken when the following conditions are fulfilled. First, the specific ionization of the atmosphere in which the readings are taken, must be the same for every observation. Second, the primary radiation falling upon the disks, for each subsequent reading, should be equal to that for the first reading, t_1.

The first of these conditions was obtained by taking all observations when the disks were in an atmosphere of dry air; no other gas being permitted in the ionization chambers. The bombardment of the plates by the X-rays, and their fatigue occurred in a specially constructed box which was so arranged, that while both plates were subject to the action of the chemically active vapor or gas, the trial plate alone was exposed to the X-rays. Thus, any change in sensitiveness, which would be caused by the exposure to the vapor itself, would be balanced; since both

plates suffered a like amount, and the fatigue noted in the observations, would be due entirely to the action of the Roentgen rays upon the trial plate.

In order to be certain that the primary radiation falling upon the disks was the same for every reading the following method was resorted to. After the original balance at the start of any series of readings had been established and the reading, t_1, taken, the disks were removed quickly from the holders and placed in the bombarding chamber. Readings were then taken to give the amount of secondary radiation for each of the holders. Thus the above mentioned second condition of refinement could be fulfilled, by simply adjusting the X-ray tube until the readings for secondary radiation from the holders, with the disks removed, were duplicated. This was, as a rule, easily accomplished and made every reading valuable.

In order to reduce possible irregularities, such as arise from a prolonged operation of the coil and tube, two sets of coils and tubes were used. One of these could be employed to fatigue the disks, which requires no absolute regularity, and the other be kept in reserve for accurate measurements.

Oxygen, chlorine, bromine, hydrogen sulphide, nitric acid and hydrochloric acid were the gases and fumes with which experiments were tried. Carbon-dioxide, which is inactive, and in the presence of which no fatigue occurs, served as a dilutent for these other highly active chemical agents. Experiments were also tried with mixtures varying in the percentage of carbon dioxide. All gases before entering the exposure chamber were carefully purified and dried.

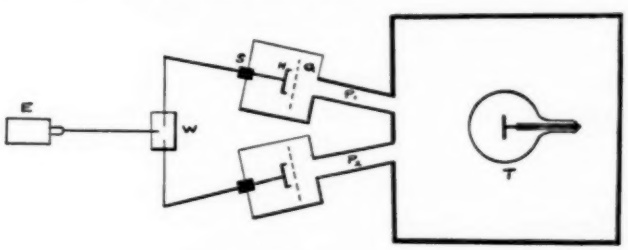


Fig. 1.

Table I. shows results for fatigue occurring in an atmosphere of almost pure oxygen; Table II. the results when about 50 per cent. carbon dioxide was present. The figures represent the percentage of radiation given off, by the fatigue plates, where 100 indicates the initial amount. In Table I., the values are the average of from two to four different series of exposures while those in Table II. are single readings.

TABLE I.

Fresh Surfaces in Pure Oxygen.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0−	100.0	100.0−	100.0−	100.0
2	100.0+	99.5−	100.0−	99.0−	99.5	100.0−
3	100.5+	99.0−	99.0−	98.0+	99.0+	99.5+
4	100.5+	99.5	99.0−	98.5−	98.5−	100.0−
5	101.0+	98.5+	99.0+	97.5	99.0−	100.0−
6	102.0+	98.5+	98.0+	96.0+	98.0−	100.0
7	101.5	———	———	———	98.0	———
8	———	98.0−	———	97.0	———	100.0−
9	102.0+	———	99.0−	97.5−	———	———

TABLE II.

Fresh Surfaces in Oxygen and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0−	100.0−	99.5−	100.0	———
2	100.0	100.0−	99.0+	99.5	100.0	———
3	100.0+	99.0+	99.0	98.0−	———	———
4	100.5	98.5+	99.0+	98.5−	99.0	———
5	101.5	99.0−	98.5−	———	97.5+	———
6	101.5−	99.0−	———	96.0−	———	———
7	———	98.5+	———	———	98.5−	100.0−
8	102.0+	———	98.5+	———	———	———
9	102.5−	99.0−	———	97.0−	———	100.0−

The formation of an iridescent film was noted in the case of the exposed copper disk. This film was always more noticeable on the days following the exposure, so the chemical action apparently persisted after the experiment. A film also formed on the standard copper plate causing it to appear dull in comparison to the other. Iron and lead also showed a small film action.

TABLE III.

Aged Surface in Chlorine and CO_2 Mixture.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0−	100.0	100.0	100.0−	100.0−	100.0
2	100.0−	100.0−	100.0+	99.0+	———	100.0
3	100.0−	100.0+	99.0+	98.0	99.0−	100.0+
4	99.5−	99.0−	100.0−	99.0−	———	———
5	99.5+	99.5	———	———	97.5−	100.0+
6	99.0+	———	100.5−	———	96.5+	100.5−
7	98.5	98.5−	———	97.5−	———	101.0−
8	99.0−	———	100.5+	97.0−	97.5	———
9	99.0−	97.0+	———	———	———	100.5+

TABLE IV.

Freshly Polished Surfaces in Cl and CO_2 Mixture.

Hours.	Fe.	Cu.	Sn.	Pb	Zn.	Al.
1	100.0−	100.0	99.0+	100.0−	100.0−	100.0
2	100.0−	99.0+	99.0−	99.0−	99.5−	100.0−
3	99.5+	98.5−	98.0−	98.0−	99.5−	———
4	99.5+	97.5	98.0	98.0+	99.0+	100.0−
5	99.0+	97.0−	98.5−	96.5	———	100.0
6	100.0−	98.0−	———	96.0−	97.0+	100.0+
7	100.0−	98.0−	98.5−	———	98.0−	100.0+
8	99.0	———	———	97.5	———	100.0−
9	99.5−	———	———	———	98.0+	100.0

Table III. shows the results when an old oxide coated surface, five to six days old, suffers fatigue in an atmosphere of chlorine and carbon dioxide; Table IV., the observations for freshly polished surfaces. In comparing the readings for iron on the two tables, it is curious to note that the old stable surface suffered a fatigue equal to one and a half per cent., while the freshly polished iron disks showed only a slight fatigue. It is possible to explain this if we remember, that in the case of an old stable oxide surface, oxidation and its accompanying increase of secondary radiation is not likely to take place. In the case of a freshly polished disk, enough air might cling to the newly formed chloride surfaces during the transfers to and from the ionization chambers, to cause an oxygen fatigue to take place along with the chlorine, and thus retard the decrease of sensitiveness due to the action of chlorine. That something of this nature must occur will be shown by the results of later experiments. According to Table III. tin and aluminum suffered an increase of sensitiveness. This was the only case in which aluminum showed any decided fatigue. Experiments were also tried for mixtures containing different percentages of chlorine. The results were practically the same as those given and were therefore not tabulated.

TABLE V.

Long Exposure in Cl and CO_2 Mixture.

Hours.	Fe.	Fe.	Fe.	Zn.	Zn.	Zn.
6	———	———	———	98.0	———	———
7	99.0−	———	———	———	———	———
8	———	98.0−	———	———	———	98.5+
9	99.0−	———	98.5−	98.5	98.0+	97.5−

Table V. shows the readings taken for freshly polished iron and zinc

disks, which were allowed to remain in the exposure chamber six hours or more, before observations were taken. In this way any oxidation due to the air in the ionization chambers was avoided. In the case of iron we see that the fatigue is decidedly greater than that given in Table IV. The fatigue for zinc was practically the same as is given in the former table.

TABLE VI.

Freshly Polished Iron in Chlorine and Oxygen Mixtures.

Hours.	5 Per Cent. Cl. Spec. I.	15 Per Cent. Cl. Spec. II.	20 Per Cent. Cl. Spec. III.
1	100.0	———	100.5
2	100.0	100.0	100.0+
3	———	99.5−	100.0
4	99.5+	99.5−	99.5+
5	100.0+	99.0	———
6	100.0−	99.5−	———
7	100.0−	———	99.5+

TABLE VII.

Disks Previously Exposed to Cl and O, in Nitric Acid.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0−	100.0	100.0	100.0−	99.5−	100.0
2	100.0−	100.0	100.0	99.5	99.0−	100.0−
3	99.5−	100.0−	———	———	———	———
4	99.0+	100.0−	100.0−	99.0+	99.5−	100.0−
5	99.5−	———	———	98.0−	———	100.0
6	———	———	———	98.5−	98.5+	———
7	———	99.5−	100.0−	———	———	100.0
8	———	———	———	———	97.0−	———
9	———	99.0	———	99.0−	———	———

TABLE VIII.

Fresh Surfaces in Nitric Acid.

Hours.	Fe.	Cu.	Sn.	Pb.	Sn.
1	100.0−	99.0−	———	99.5−	99.0−
2	100.0−	98.0−	———	99.5+	99.0−
3	100.0−	97.0+	———	———	———
4	99.5−	97.5	99.0+	99.5	99.5
5	99.0−	97.0+	———	99.0	99.5−
6	99.5−	96.0−	100.0−	———	99.0+
7	99.0	96.0−	100.0+	99.0−	———
8	———	———	———	98.0−	98.5−
9	98.0−	———	———	———	———

Table VI., which shows the results for three series of readings taken

for mixtures of oxygen and chlorine, indicates that hardly any fatigue takes place in this atmosphere. Mixtures varying in chlorine from five to twenty per cent. were used. This table substantiates the former proposed theory, namely that for a mixture of two chemically active gases a double fatigue may take place. In this case the oxygen by Table I. would cause an increase in sensitiveness while the chlorine according to Table V. a decrease. The two fatigues occurring at the same time would counteract each other and hence no change of sensitiveness would be noted.

The readings in Table VII. give the fatigue of metals which had previously suffered exposure in both chlorine and oxygen, and were then fatigued in an atmosphere of carbon dioxide and nitric acid fumes. The lead and zinc disks, although thickly coated with films due to the chlorine and oxygen, show a decided change of sensitiveness.

Table VIII. gives the results for freshly polished disks fatigued in an atmosphere of carbon dioxide which had passed over fuming nitric acid. Copper showed a very noticeable fatigue and also a decided film action.

TABLE IX.

Fresh Surfaces in Bromine and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.	Al.
1	100.0	100.0−	———	100.0−	100.0	100.0
2	100.0	100.0−	100.0−	99.5	100.0	100.0−
3	100.0−	100.0−	99.5−	99.5−	———	———
4	100.0−	———	———	99.5−	100.0−	———
5	———	99.5−	100.0−	———	———	———
6	100.0+	———	99.0−	99.0+	100.0−	100.0−
7	———	99.5−	98.5−	———	100.0−	———
8						
9						

TABLE X.

Fresh Surfaces in HCl Fumes and CO_2.

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.
1	100	100	100.0	100.0	100.0
2	100	———	99.0−	100.0	100.0−
3	99.5	99.0−	99.5−	99.5+	99.5−
4	99.5−	98.0−	99.5−	99.5+	99.5−
5	———	98.0	98.5	100.0−	———
6	99.0+	96.5−	98.0−	99.0+	
7	99.5	96.0	98.0−	———	99.0
8	———	96.5−	———	99.5−	———
9	———	———	97.0−	———	99.5−

Tables IX. and X. give the fatigue for disks with fresh surfaces, exposed

in bromine vapor and CO_2. While bromine caused a decided film action, hardly any fatigue was noted except in the case of tin. The fatigue occurring in hydrochloric acid fumes was about equal to that for chlorine gas, copper giving a slightly greater change for the fumes.

TABLE XI.

HCl Coated Disks in Hydrogen Sulphide and CO_2

Hours.	Fe.	Cu.	Sn.	Pb.	Zn.
1	100.0	100.0	100.0−	99.5	100.0
2	100.0	100.0−	100.0—	99.0−	100.0
3	100.0−	98.5	100.0−	———	99.0+
4	100.0	99.0+	99.5−	98.0−	98.5−
5	100.5+	99.5−	98.5−	97.5+	99.0
6	100.0	98.5	98.0	96.5	———
7	———	98.0	98.0	98.5+	———
8					
9					

TABLE XII.

Freshly Polished Disks in H_2S and CO_2.

Hours.	Fe.	Cu.	Pb.	Zn.
1	100.0	100.0	100.0	99.0+
2	100.0	100.0	99.5−	98.0−
3	100.5+	100.0	98.0−	98.0−
4	100.5	98.5+	96.5−	98.0−
5	———	98.0−	95.0	———
6	101.0+	97.0	95.0−	———
7	101.0+	97.5−	95.0−	98.0+
8	———	98.5−	94.5−	———
9				

Tables XI. and XII. show results for exposure occurring in atmospheres of H_2S and CO_2. Freshly polished lead, immersed in hydrogen sulphide, gave the greatest fatigue of any metal in any gas. The readings given for lead are the averages of three series of observations. The film action for hydrogen sulphide was very noticeable for every metal.

SUMMARY OF RESULTS.

Fatigue occurred when freshly polished surfaces of iron, copper, tin, lead, and zinc were exposed to X-rays, in the presence of oxygen or a mixture of oxygen and carbon dioxide. Aluminum showed no appreciable change. The fatigue for metals exposed in an atmosphere of pure oxygen was practically equal to that which occurred when fifty per cent.

CO_2 was present. It was also found that the changes in secondary radiation of all metals in chlorine and CO_2 were pratically of the same amount, although the percentage of the mixture was varied through rather wide limits.

Old oxide surfaces, which are stable so far as fatigue in an atmosphere of oxygen is concerned, showed decided fatigue when tested in chlorine.

In the case of iron exposed in an atmosphere of chlorine and oxygen, a double fatigue seemed to take place, one tending to increase and the other to decrease the radiation.

Fatigue was found for metals with freshly polished surfaces when exposed in chlorine, bromine, nitric acid fumes, hydrogen sulphide, and hydrochloric acid. In some cases, surfaces which had undergone a previous chemical combination, showed a further combination and fatigue when exposed to another chemical agent and the X-rays.

No relation has been found between the amount of fatigue for a metal and the corresponding activity of chemical action of the gas and the metal.

In conclusion I wish to extend to Professor More my sincere thanks for his advice and many suggestions during this work and also acknowledge the assistance rendered by the grant from the Bache Fund of the National Academy of Sciences.

UNIVERSITY OF CINCINNATI,
June, 1911.

NEW RECORDS OF SOUND WAVES FROM A VIBRATING FLAME.

BY JOSEPH G. BROWN.

VIBRATING flames are commonly classified as singing flames sensitive flames, and manometric flames. The singing flame was first observed by Higgins[1] in 1777, soon after the discovery of hydrogen. The term singing flame is now usually limited to flames which vibrate in a pipe or other resonator. The sensitive flame was first observed by LeConte[2] in 1858, and any naked flame which vibrates under the action of sound waves is termed sensitive. In 1862 Koenig[3] devised his manometric capsule, and he called the flame which was made to vibrate by means of the capsule a manometric flame.

In the study of vibrating flames two distinct optical methods have been employed. The method of the revolving mirror was first applied by Wheatstone[4] in 1834 to the singing flame. Tyndall,[5] Barrett,[6] and others made observations by this method upon both the singing and sensitive flames.

The stroboscopic method of observation was devised by Toepler[7] in 1866. As a means of examining the action of the vibrating flame this method is unsurpassed; because the different phases of the vibration may be observed and studied at will, and made to succeed each other at any desired rate.

FLAME PICTURES.

When Koenig devised his manometric flame he used the revolving mirror method of observation and called the view which he thus obtained a flame picture. In his attempt to analyze the vowel sounds, Koenig[8] sketched a number of these flame pictures. Later, the flame pictures were photographed by Doumer,[9] Merritt,[10] Hallock,[11] Nichols and Merritt,[12] and Austin.[13]

It is very evident that the flame pictures are in no sense time-displacement diagrams of the sound waves producing them. They are

[1] Nicholson's Jour., 1, 129, 1802.
[2] Am. Jour. of Sci., 75, 62, 1858.
[3] Pogg. Ann., 122, 242, 1864.
[4] Phil. Trans., 1834, p. 586.
[5] Phil. Mag. (4), 13, 473, 1857.
[6] Phil. Mag. (4), 33, 26, 1867.
[7] Pogg. Ann., 128, 126, 1866.
[8] Phil. Mag. (4), 45, 1 and 105, 1873.
[9] Phil. Mag. (5), 22, 309, 1886.
[10] PHYS. REV., 1, 166, 1893.
[11] PHYS. REV. 2, 305, 1895.
[12] PHYS. REV., 7, 93, 1898.
[13] PHYS. REV., 12, 121, 1901.

overlapping images of successive phases of the vibrating flame, and the wave form can only be inferred approximately from such a result. The luminous tip of the vibrating flame is not a definite thing which vibrates vertically. The stroboscopic observations of Toepler[1] and the photographs of Marbe and Seddig[2] show that the flame consists of alternating expansions and contractions which continually move upward and burn out as they rise. The expansions are much brighter than the contractions and often are the only luminous parts of the flame. If the variations in pressure are quite small as compared with the mean pressure of the gas, the shape of the flame changes very little and the tip executes a vertical vibration. In this case, the flame picture approaches a time-displacement diagram, but the distortion due to the upward moving enlargements and contractions is always noticeable. If the variations in pressure are large, the change in shape of the flame is very marked, the tip becoming mushroom shaped. Or if the change in pressure is large and sudden, a vortex ring is formed which separates entirely from the main body of the flame.

On account of this complicated action of the vibrating flame, the flame pictures have never been very successful as a means of analyzing sound waves. Some time ago it occurred to me that certain modifications in the flame and in the method of making observations, might result in obtaining a time-displacement diagram which would give the wave form with considerable accuracy. The chief object of this paper is to describe some attempts which I have made with this object in view, and to present some of the records obtained.

My plan has been to vibrate a flame with sound waves of known form and then to modify the conditions until the wave form was obtained. The sound wave from a telephone receiver vibrated by the alternating current of the lighting circuit, was used as a standard source for all preliminary trials. The arrangement was very similar to that used by Austin,[3] and later by Marbe.[4] The oscillograph record of this circuit was extremely close to a sine curve, and the vibration of the telephone disc, when tested by the method of D. C. Miller,[5] was found to be almost simple harmonic.

Smoke Records.

The first modification which I tried suggested itself to me while I was repeating the smoke ring experiment of Marbe.[6] This consisted in

[1] Loc. cit.
[2] Wied. Ann. (4), 30, 579, 1909.
[3] Loc. cit.
[4] Phys. Zeit., 7, 543, 1906.
[5] Phys. Rev., 28, 151, 1909.
[6] Loc. cit.

projecting the jet tube at a considerable angle away from the vertical, keeping it perpendicular to the direction of motion of the paper, and allowing the tip of the smoky acetylene flame to come in contact with the paper. My idea in doing this was that the variations in pressure which tend to lengthen and shorten the flame might give the tip a transverse vibration which would be indicated by the deposit of soot. I soon found that with proper adjustment of the jet the soot was deposited upon the paper in lines and bands. (See Fig. 1.) A very fine line (*a*) was formed by a thread of soot which appeared to come from the center of the flame. A coarser line (*b*) was formed by a thread of soot which came from the forward side of the flame; *i. e.*, from the side in the direction in which the paper was moving. A similar thread came from the backward side of the flame, but it was not deposited upon the paper. A heavy, narrow band of soot (*c*) was deposited from the near side of the flame; *i. e.*, from the side nearest the jet; and a light, broad band (*d*) came from the far side of the flame. This result was obtained with a jet tube having an opening about 1 mm. in diameter, projected about 65° away from the vertical, with the opening about 2 cm. from the paper, and with a gas pressure of about 2 mm. of water. The paper was in the form of a belt upon two brass drums. One drum was rotated by an electric motor and the flame was placed under the other drum. The paper moved past the flame with a velocity of about 75 cm. per second. When the flame was vibrated by the telephone receiver the lines and bands of soot were deposited as shown in the right half of Fig. 1. It will be noticed that the fine line (*a*) indicates only the longitudinal vibration of the flame and comes the nearest to being a sine curve, hence represents most nearly the form of the sound wave. The coarse line (*b*) indicates the longitudinal vibration of the flame fairly well but it is not a sine curve, the distortion being due to the expansions and contractions of the flame. This distortion might be expected from the fact that this line is deposited from the edge of the flame, while the fine line is deposited from the center of the flame. The narrow band (*c*) shows the longitudinal vibrations to some extent, but on account of the transverse vibration the soot from the band is deposited heavier on certain areas when the relative velocity between the edge of the flame and the paper is small, and lighter on other areas when the relative velocity is large. This produces an interesting pattern which characterizes the vibration but is difficult of interpretation. The broad band of soot (*d*) shows this effect of the transverse vibration to a marked extent. I am inclined to think that the formation of the rings observed by Marbe is explained in the same way.

Unfortunately the fine line does not stand out by itself but is partly

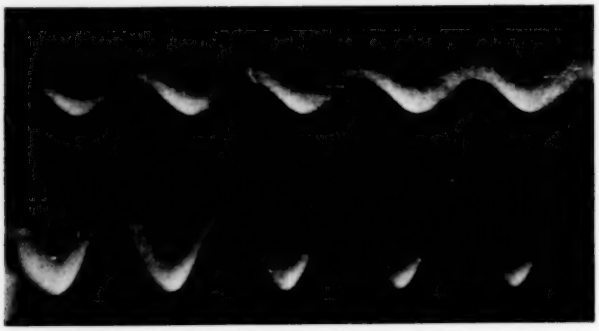


Fig. 8.

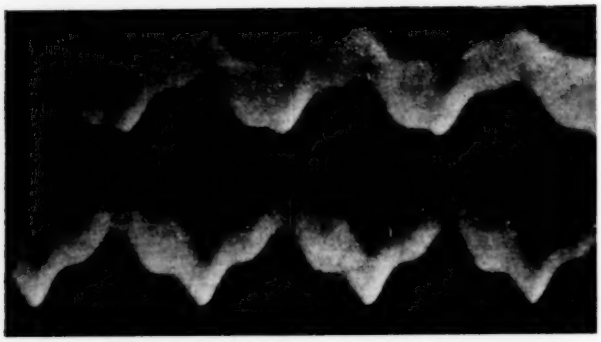


Fig. 9.

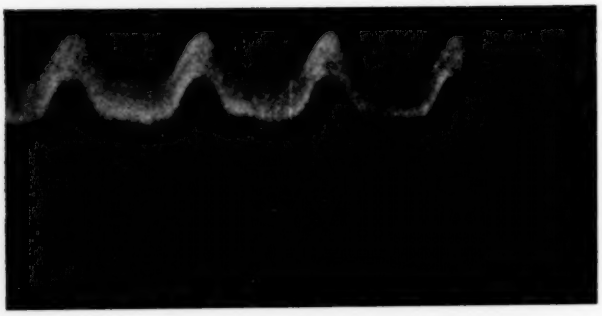


Fig. 10.

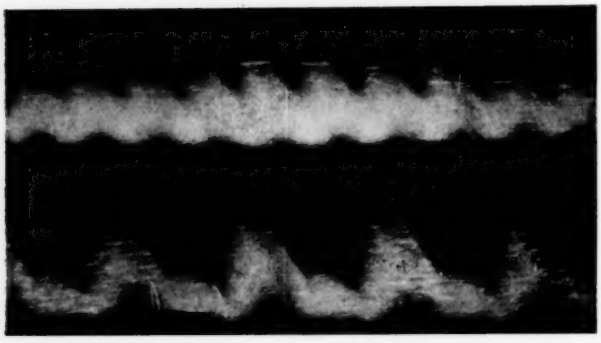


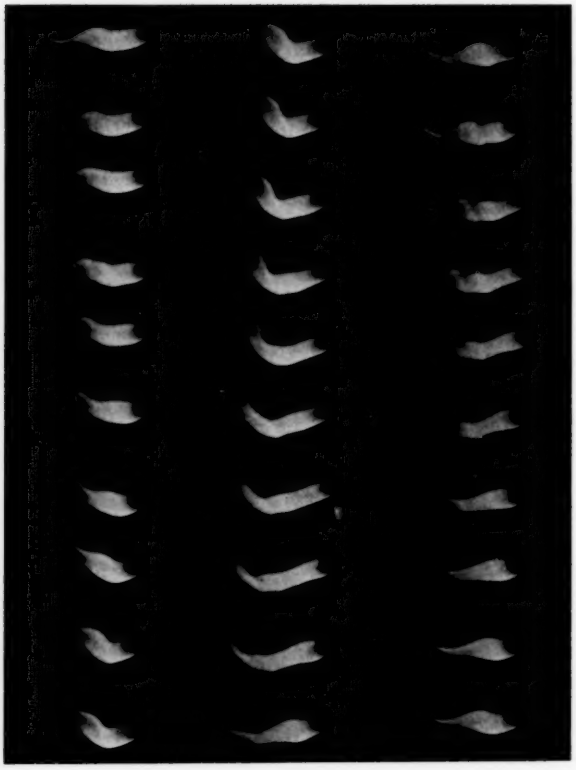
Fig. 11.

F. G. BROWN.

PLATE III.

Fig. 5.

Fig. 6.



a *b* *c*

Fig. 7.

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PLATE II.

Physical Review.
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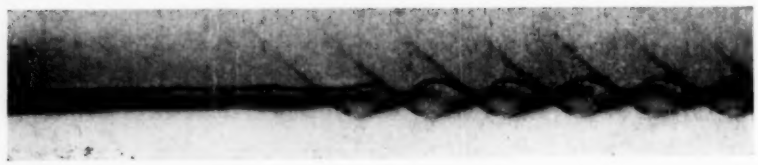

Fig. 1.

Fig. 2.

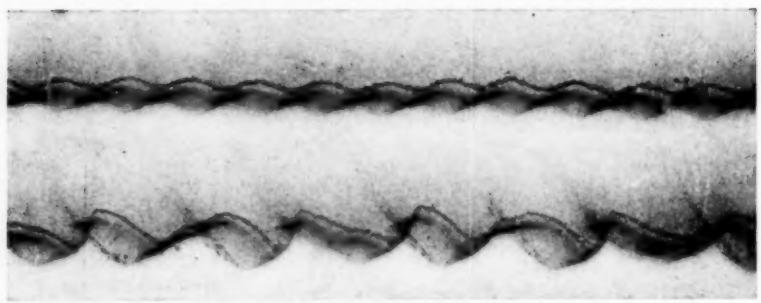

Fig. 3.

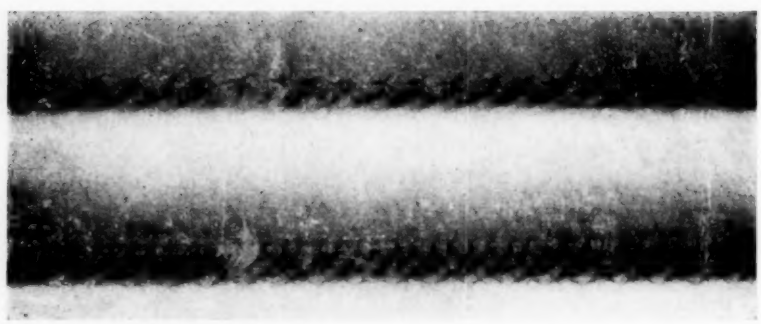

Fig. 4.

F. G. BROWN.

PLATE I.

covered by soot from the other sources. This can be avoided by using a greater gas pressure and consequently a larger flame, but the sensitiveness is greatly reduced. Fig. 2 shows the result of this adjustment.

A few records from other sources will serve to show the extent to which this method will reproduce complicated wave forms. The smoke record of an electrically vibrated tuning fork ($n = 100$) placed in front of a Koenig capsule, is shown in Fig. 3 (*a*). The result of the composition of this fork with the alternating current ($n = 61$) is shown in Fig. 3 (*b*). A record of sung vowels is shown in Fig. 4; (*a*) is "e" as in "he," and (*b*) is "a" as in "hay."

Photographic Records.

The second modification was suggested by the fact that the lower luminous edge of the projected flame seemed to be exceedingly sharp and to vibrate with considerable amplitude. This was especially noticeable when the jet tube was projected about 45° below the horizontal and a small quantity of illuminating gas was mixed with the acetylene to keep the flame from smoking. Fig. 5 is a photograph of such a flame when steady, and Fig. 6 is the same flame while being vibrated by the alternating current. When this vibrating flame was examined with a stroboscope, it was very evident that the longitudinal vibration at the base of the flame was very largely carried over into a transverse vibration of the luminous part of the flame. This is strikingly shown by a series of photographs of the flame secured by means of a coupled stroboscope and piston, a device designed by Prof. G. S. Moler and kindly placed at my disposal for this purpose. Fig. 7 shows thirty successive phases covering one complete vibration of the flame.

When a narrow slit was placed before the flame so that the slit was perpendicular to the lower luminous edge, and the motion was examined by means of a revolving mirror having its axis parallel with the slit, it seemed probable that with proper adjustment of the slit a very good photographic record could be obtained. Accordingly a revolving film was arranged in a box so that an exposure could be made through a very narrow slit placed just in front of the film. The box was arranged so that it could be adjusted for focus and for position of the slit across the image of the flame. A shutter was connected with the wheel which carried the film in such a way that the exposure could be made at any time upon any quarter of the film.

Fig. 8 shows the result obtained from the telephone receiver with two different values of the alternating current. The boundary line which indicates the motion of the lower edge of the flame is very close to a sine curve. Curve (*a*) happened to be of such amplitude that it could be

compared with Fig. 2 by superposition. The agreement was remarkably good, thus showing that both methods give the same wave form, and presumably the correct wave form of the source used.

Fig. 9 shows two curves from the telephone made to vibrate with another alternating current. The frequency of this current was 20, and it contained a very marked third harmonic. In (*b*) the phase of the harmonic was advanced 180° from what it was in (*a*).

Fig. 10 shows curves from the piston referred to above. In (*b*) the frequency was much greater than it was in (*a*). The peculiar form of these curves is due to the fact that the piston was vibrating in a cylinder closed at one end, and that the gas could leak around the piston. Record (*b*) is the curve which represents the vibration, the phases of which are shown in Fig. 7.

For the sake of comparison I have included photographs of two flame pictures. Fig. 11 (*a*) is the flame picture obtained when the telephone receiver is vibrated by the lighting current, and corresponds to the records shown in Fig. 2 and in Fig. 8. Fig. 11 (*b*) is the result when the piston vibrator is used, and corresponds to the record shown in Fig. 10 (*b*).

CONCLUSION.

It is doubtful whether the curves obtained from the vibrating flame by either of the above methods will serve as well as other means for analyzing sound waves. The curves shown by Professor D. C. Miller at the April, 1911, meeting of the Physical Society show far more promise for this purpose. As records from a vibrating flame, however, it is believed that they are of far more value than are any records heretofore obtained.

In all devices so far used in the analysis of sound waves, a correction must be made for the resonance effects, due to the free periods of the recording system, before the analysis is complete. In the case of the flame made to vibrate with the manometric capsule these effects are very small but certainly are not negligible. The preceding experiments show that a flame, made to vibrate by the variations in pressure of a sound wave within the gas jet, can be made to reproduce the curve which represents the form of the sound wave. If the flame could be made to vibrate with sufficient intensity by the variations in pressure of a sound wave in the free air outside of the gas jet, the resonance effects would be almost, if not wholly, eliminated. The observations of Marbe[1] and the results of some experiments which I have recently made seem to show that there is a possibility of accomplishing this result.

STANFORD UNIVERSITY,
August, 1911.

[1] Phys. Zeit., 8, 92, 1907.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FIFTY-EIGHTH MEETING.

THE regular fall meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 14, 1911, with President W. F. Magie in the chair.

The following papers were presented:

A Study of Simultaneous Tracings from the Apex of the Heart and the Radial Artery with the Micrograph. ALBERT C. CREHORE.

Torsional Rotatory Polarization. ARTHUR W. EWELL.

Spectral Luminosity Curves Determined by the Method of Critical Frequencies. HERBERT E. IVES.

A New Form of Gold Leaf Electroscope: A Null Instrument. J. C. HUBBARD.

The Electron Theory of Voltaic Force and Thermo-electricity. O. W. RICHARDSON.

The Influence of the Contact Difference of Potential between the Plates Emitting and Receiving Electrons liberated by Ultra Violet Light. K. T. COMPTON.

A Study of Tracings from the Region near the Apex of the Heart. ALBERT C. CREHORE.

A Study of the Presphygmic Period with the Micrograph. ALBERT C. CREHORE.

The Positive Ionization from Hot Salts. O. W. RICHARDSON.

On the Distribution and Direction of Motion of the Interference Bands of Light Formed by Thin Plates as the Thickness of the Plate Varies. ALBERT C. CREHORE.

A New Virial Theorem. D. F. COMSTOCK.

The Effect of Pressure on the Liquid and Five Solid Forms of Water. P. W. BRIDGMAN.

A Method of Determining Mean Reflection Coefficients. W. S. FRANKLIN and J. H. WILEY.

At the close of the program the meeting discussed briefly, in committee of the whole, the relations between the Society and the PHYSICAL REVIEW, Mr. Franklin acting as chairman. When the committee rose the chairman announced the adoption of the following resolutions:

1. *Resolved*, that this meeting requests the council to present to the society a plan by which the society shall publish a journal.

2. *Resolved*, further, that the council be requested to enter into negotiations with the editors of the PHYSICAL REVIEW to determine under what conditions the control of the REVIEW may be transferred to the society.

Adjourned at 1:30 P.M.

ERNEST MERITT,
Secretary.

THE ELECTRON THEORY OF CONTACT ELECTROMOTIVE FORCE AND OF THERMOELECTRICITY.[1]

BY O. W. RICHARDSON.

A DISCUSSION of the nature of contact electromotive force and of the laws of thermoelectricity on the view that metals contain a large number (n per c.c.) of free electrons, dynamically equivalent to the molecules of a gas, which are retained in the metal by the action of forces near the boundary giving rise to work functions, w_1, w_2, etc., characteristic of each metal. This hypothesis has already been very successful in accounting for the laws which regulate the emission of negative electrons from hot bodies. Extensive use is also made of the theorem which has been proved by writers on the kinetic theory with sufficient generality to cover the conditions postulated, that if W is the work done in taking an electron from a point A to a point B then

$$W = R\theta \log \frac{n_1}{n_2},$$

where R is the gas constant calculated for a single molecule, θ is the absolute temperature, and n_1 and n_2 are the concentrations of the free electrons at A and B respectively.

By considering the case of a number of electrons in a thermally and electrically insulated enclosure it is shown that the condition for equilibrium is the invariance of $w_A - eV_A - R\theta \log n_A$ for every point A in the enclosure: where e is the charge of an electron, V_A is the electric potential at A and w_A is the work done by an electron in escaping from the metal in which A is. If A is in the space between the conductors $w_A = 0$. It follows that there is a permanent difference of electric potential $V_m - V_g$ between any two conductors which is given by

$$V_m - V_g = \frac{1}{e}\left\{w_m - w_g + R\theta \log \frac{n_g}{n_m}\right\}$$

Experimental indications are that $w_m - w_g$ is much larger than the logarithmic term and is in all probability comparable with the observed Volta effects. If more complete knowledge of the values of the w's confirms these indications it would follow that the observed contact differences are intrinsic properties of the metals and not due to chemical action. Several weak points in the current evidence in favor of chemical action are pointed out.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

By considering the transportation of a number of electrons around suitable circuits of different metals and at different temperatures, so that the transference is partly along connecting conductors and partly through the surrounding space, but always in a resverible manner, it is shown that:

$$\pi e = R\theta \log \frac{P_2}{P_1} = R\theta \log \frac{n_2}{n_1},$$

$$\sigma = \frac{1}{\epsilon}\left\{\frac{Rr}{\gamma - 1} - R\theta \frac{d}{d\theta}\left(\log \frac{P}{P_o}\right)\right\} = \frac{1}{\epsilon}\left\{\frac{R}{\gamma - 1} - R\theta \frac{d}{d\theta}\left(\log \frac{n}{n_o}\right)\right\},$$

$$Te = R\int_{\theta_0}^{\theta'} \log\left(\frac{P_2}{P_1}\right) d\theta = \epsilon \int_{\theta_0}^{\theta'} \frac{\pi}{\theta}\, d\theta,$$

$$\frac{dT}{d\theta} = \frac{R}{\epsilon} \log \frac{P_2}{P_1} = \frac{\pi}{\theta} = \frac{R}{\epsilon} \log \frac{n_2}{n_1},$$

where π is the Peltier effect between the metals 1 and 2 at temperature θ, P_2 and P_1 are the respective pressures of the free electrons inside the same metals, n_2 and n_1 are the corresponding concentrations, σ is the specific heat of electricity, γ is the ratio of the specific heats of the electrons at constant pressure and constant volume, n_0 and P_0 are concentration and pressure of the internal free electrons at a fixed temperature θ_0, and n and P the corresponding quantities at the variable temperature θ. Finally T is the thermoelectromotive force of a circuit of the metals 1 and 2 whose junctions are at θ' and θ_0 respectively.

These formulæ agree with the results of Lord Kelvin's theory of thermoelectric phenomena, but they are not in entire accordance with formulæ which other writers on the electron theory have deduced by using other methods. Reasons are given, however, for believing them to be correct.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

THE INFLUENCE OF CONTACT DIFFERENCE OF POTENTIAL ON THE MEASUREMENT OF ELECTRON VELOCITIES IN THE PHOTO-ELECTRIC EFFECT.[1]

BY KARL T. COMPTON.

THE writer finds that when the velocities of the electrons liberated from metals by ultra-violet light are determined in the usual way, *i. e.*, by the relation

$$v = \sqrt{\frac{2P\epsilon}{m}},$$

where ϵ and m are the charge and mass associated with an electron and P is the greatest retarding difference of potential against which the electron can escape from the emitting plate, the results are incorrect unless the contact

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

difference of potential between the emitting and receiving plates is added to the externally applied difference of potential.

The following results are established.

I. When electron reflection is prevented by the use of a perforated screen and an auxiliary field, there is a shift of the "distribution of velocity" curves due, probably, to stray field through the perforations. This can be corrected for.

II. The contact difference of potential between the emitting and receiving plates must be added to the applied difference of potential when making measurements of the electron velocities.

III. When this contact difference of potential is corrected for, it is found that aluminium, zinc, brass, copper and platinum emit electrons with equal velocities.

IV. The shift of the "distribution of velocity" curves with the time since polishing the plates is accounted for by the time changes in the contact difference of potential between the plates.

The above results were obtained with plates tested in a high vacuum within a reasonably short time after polishing.

The writer expresses his indebtedness to Professor O. W. Richardson for his suggestions and advice during the investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

THE POSITIVE IONIZATION FROM HOT SALTS.[1]

BY O. W. RICHARDSON.

THE paper describes experiments by the author which, together with those of Dr. C. J. Davisson,[2] show that the positive ions emitted by salts are metallic atoms which, in almost every case, carry a single electronic charge. The only indication of multiple charges is in the case of certain zinc salts where there is some evidence of the occurrence of positive ions with a charge equal to $2e$. The nature of the ions emitted by the salts is independent of the nature and pressure of the surrounding gas at low pressure, but it is necessary, in order to account for the values of e/m given by a number of salts such as aluminium phosphate, to suppose that the ions they emit do not come from the salt itself but from some impurity with which it is contaminated. Generally speaking the contaminations seem to be salts of the alkali metals, which are very efficient emitters.

The ionization produced by a large number of salts has been examined in gases (chiefly in air, however) at different pressures. The results are very complex and indicate that it is almost impossible to dednce anything as to the

[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

[2] PHYS. REV., June, 1911.

nature of the ions from experiments of this character. A specimen of pure aluminium phosphate has been prepared which shows a very small ionization in comparison with either ordinarily pure aluminium phosphate or with the salts of the alkali and alkaline earth metals at the same temperature.

With some salts under certain conditions the decay of the positive ionization depends on the electrical field employed as well as on the time. A similar effect has already been shown by the author to characterize the positive ionization emitted by "new" platinum wires.

There is some indication that the action of vapors emitted by the salts on the hot platinum present in the apparatus is an important factor in the emission.

Torsional Rotatory Polarization.[1]

By Arthut W. Ewell.

EXPERIMENTS which have been reported upon previously,[2] demonstrated that torsional rotatory polarization is a joint effect of the twist and the accompanying transverse distortion. The latter produces double refraction and the former rotates the axes of this double refraction into an helical configuration. The theory of the phenomena has been worked out and the relation between the total difference of phase due to this double refraction (irrespective of the helical arrangement), the total angle of twist, and the rotation, may be expressed graphically. If a segment of a circle be constructed of aperture equal to twice the total twist, and whose arc is equal to the total difference of phase (in radians), the area of the segment is numerically twice the rotation (in radians).

It is difficult to measure the relative distortion of a twisted cylinder, and therefore cylinders were formed with an initial helical structure. The section was rectangular (to obtain simple strains), and when they were compressed at each point perpendicular to two of the opposite sides, they resembled optically and mechanically a twisted cylinder. For each such helical cylinder was prepared a similar straight cylinder which was compressed an equal amount. The difference of phase in the latter and the rotatory polarization of the former were observed. The observed rotations always agreed, within the limits of experimental error, with the rotation calculated by introducing the observed difference of phase and the angle of twist into the above graphical construction.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, Oct. 14, 1911.

[2] Am. Jo. of Science, VIII., 1899, p. 89; XV., 1903, p. 363; Phys. Zeit. I., 1899, p. 201; V., 1903, p. 706; Johns Hopkins Univ. Cir., 1900, p. 64; Phys. Rev., XXXI., 1910, p. 607.

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